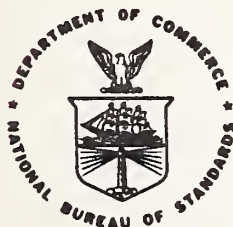NBSIR 78-1509

An Algorithm and Basic Computer Program for Calculating Simple Coal Gasification Equilibria

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INTRODUCTION

Designing plants for the gasification of coal is being aided by
testing materials expected to be capable of withstanding the required
conditions. A variety of physical and chemical tests are performed
under these possible conditions and in the same gaseous environments.
Generally, however, to fully understand the observed effects, tests are
made in a variety of environments related to those of the gasification
plants and at a variety of conditions of temperature and pressure. The
gas mixtures used as the environments are generally not at chemical
equilibrium, and depending upon the conditions and the possible presence
of catalyzing substances, chemical reactions will take place [2] at some
unpredictable speed. The tester is concerned about the true nature of
the environment, but this can only be found by carefully arranged chemical
analyses. On the other hand it is of value to know the maximum change
that can occur during the test. This can be determined if the equi-
librium composition for the mixture can be calculated.

This report is concerned with a simple procedure for calculating the equilibrium composition of such testing mixtures. The aims in devising this procedure were to provide an interactive computer program that was easy to use, not inherently complex, that exploited the relative simplicity of the BASIC programming language, and was confined to the coal gasification problem alone. Such a program would be usable by non-programmers, who merely need to sign on an interactive timesharing terminal and type answers to a few questions about the testing conditions. There are batch programs already available for solving simultaneous chemical equilibria, e.g., CEC71 [8], however these have many disadvantages for the problem at hand. They are often complex, handle many more problems than are needed, require extensive storage, have excessive print-out, and require some learning prior to use. There is an interesting algorithm [14] with a computer program written in ALGOL, which treats multiphase chemical equilibria involved in coal combustion. This includes formation of slag.

The development of a program fulfilling these aims is presented here. Included are the mathematical and chemical thermodynamic treatment. Instructions for use and a listing are provided. Also included are some results obtained using the program which illustrate the use of the phase rule to predict the potential condensation of solid carbon during a materials test under coal gasification related conditions.

The program, called COLGAS, is capable of calculating equilibrium gas compositions containing CH_4, CO, CO_2, H_2, and H_2O as well as the quantity of solid carbon and/or liquid water when these are present.

Constant temperature is assumed, but the operator may choose to hold either pressure or volume constant.

The exposition may appear more detailed than is warranted for the simplicity of the problem to which the development is applied. The author found this to be helpful in seeing the relationship of the parts and the exact nature of the assumptions used. The detail has been retained in the report with the hope that some readers may benefit thereby.

Wherever possible the recommendations of The International Union of Pure and Applied Chemistry (IUPAC) for physicochemical symbols and units [3] have been followed. This includes the SI units. However, the atmosphere, liter, and degree Celsius have been made usable. The SI units used are the megapascal (MPa) and the kelvin (K). Because of the desire to keep symbolism the same in the text and in the computer program wherever possible, occasionally the IUPAC symbol has not been used. For example, k is used for equilibrium constant rather than K.

THERMODYNAMIC BASIS AND ASSUMPTIONS

The literature dealing with calculation of chemical equilibrium compositions is abundant, and most of it up to 1970 is given by van Zeggeren and Storey [9]. Other useful reviews are by Zeleznik and Gordon [13] and Klein [18]. The two known approaches depend upon either solving simultaneous equilibrium constant equations or minimizing the Gibbs energy of the system (for a constant pressure problem). Both include the constraints for conserving the chemical elements. The first of these methods is rather old, but Brinkley [10] is credited with developing a generalized scheme for a systematic treatment using equilibrium constants. This procedure is amenable to the use of computers. The first reference to minimizing the Gibbs energy as a route to solving simultaneous chemical equilibria was probably by White, Johnson, and Dantzig [11]. In principal, however, these two approaches are equivalent. This becomes obvious if minimization is effected by setting the partial derivatives with respect to the constituents equal to zero. The result is a set of equations involving the logarithms of the species concentrations. If logarithms are taken of the Brinkley equilibrium constant equations a set of similar equations is obtained. With a certain choice of "constituents" in the Brinkley sense, these sets of equations are identical. A real difference in the methods can occur if minimization is effected by other methods such as steepest descent or linear programming [11].

Minimization of the Gibbs energy by use of the partial deriviatives has at least one advantage over the Brinkley method. There is no need

to choose substances likely to be present in larger abundance than others and to treat these differently. All substances in the gas phase are treated alike and therefore the algorithm can be a bit less complex. Furthermore, the addition of a new substance is always done in the same way and does not lead to rewriting the equations already in the algorithm. Only new equations are added. For these reasons minimizing the Gibbs energy was the chosen method. Minimization is accomplished by the use of Lagrangian multipliers and setting the partial derivatives equal to zero followed by the Newton-Raphson method of solution. Minimization of the Helmholtz energy for constant volume problems leads to equations only slightly different from those for constant pressure and to minor additions to the program.

For the testing of coal gasification plant materials a reference environment has been chosen [12] and is shown in Table 1.

Table 1.   Standard Gas Environment

Volume Percent

CH_4	CO	CO_2	H_2	H_2O	H_2S	NH_3
5	18	12	24	39.5	0.5	1

The presence of H_2S can lead to SO_2 and the NH_3 can give N_2. However, all four of these will be in relatively low concentration and it was decided to consider the first five species only. If desired, the concentrations of the others can be simply calculated once these five are known, as well as the amount of sulfur and/or nitrogen.

All gases are assumed to be ideal. Condensed water and carbon are assumed to be pure. For example, the solubility of carbon dioxide in water is ignored. For constant volume problems, the volume of condensed species is ignored in comparison to the gas volumes. That this is generally acceptable is evident from the fact that when 90% of the original gas has been equilibrated as condensed species, these latter contribute only about 0.5% to the total volume in the worst case.

THERMODYNAMIC AND MATHEMATICAL TREATMENT

Assume a system of s substances, g of which are gases, at pressure P, with volume V, and thermodynamic temperature T. If the system is not at chemical equilibrium, chemical reactions will adjust the number of moles of each substance, n_i, until equilibrium is attained. At this point the Gibbs energy, G, will have become a minimum if the pressure and temperature are kept constant (ref 1, p 209). If, instead, the volume and temperature are kept constant, the Helmholtz energy, A, will have become a minimum, (ref 1, p 208). The s-g $\geq$ 0 substances are condensed phases and are assumed to be pure and immiscible with one another. The gases are assumed to be ideal and insoluble in the condensed phases.

The Gibbs energy may be expressed as the sum of the contributions from each substance.

$$G = \sum_{1}^{s} n_i \mu_i \tag{1}$$

The μ_i are Gibbs energies per mole and are known as the partial molar Gibbs energies or the chemical potentials (ref 1, pp 214,215). For the g gases in an ideal mixture the chemical potentials are a function of the partial pressures, p_i (ref 1, p 261).

$$\mu_i = \mu_i^o + RT \ln p_i \tag{2}$$

The μ_i^o are constants at fixed temperature and represent the Gibbs energy of one mole of pure ideal gas at 0.101325 megapascals (one atmosphere) pressure. For pure condensed phases the μ_i are merely the μ^o for these substances. Consequently, equation (1) can now be rewritten.

$$G = \sum_1^s n_i \mu_i^o + RT \sum_1^g n_i \ln p_i \qquad (3)$$

Note that the first g subscripts have been assigned to the gases. The partial pressures are equal to the product of the mole fractions, n_i/n_g, and the total pressure.

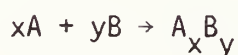$$p_i = (n_i/n_g) P \qquad (4)$$

$$n_g = \sum_1^g n_i \qquad (5)$$

Thus, equation (3) may be rewritten.

$$G = \sum_1^s n_i \mu_i^o + RT \sum_1^g n_i \ln (n_i P/n_g) \qquad (6)$$

The μ_i may be evaluated by considering compounds. For example, the compound $A_x B_y$ may be made, in principle, from its elements, A and B, according to the following chemical reaction.

$$xA + yB \rightarrow A_x B_y$$

The Gibbs energy change for the reversible formation of one mole of A_xB_y is given by ΔG_f^o with all the substances in the standard states (ref 1, p 283).

$$\Delta G_f^o = \mu_{A_xB_y}^o - x\,\mu_A^o - y\,\mu_B^o$$

But for an equilibrium among these three substances, the ΔG_f^o is related to the equilibrium constant (ref 1, p 283).

$$\Delta G^o = -\,RT\,\ln k_f$$

Here k_f is the equilibrium constant for formation of one mole of substance A_xB_y, and R is the molar gas constant. Consequently, one can express the chemical potential of a compound in terms of the absolute chemical potentials of its elements and the equilibrium constant of formation.

$$\mu_{A_xB_y}^o = x\,\mu_A^o + y\,\mu_B^o - RT\,\ln k_f$$

For the general case let k_i represent the equilibrium constant of formation for the i-th substance.

$$\mu_i = \sum_{j=1}^{e} \nu_{ij}\,\mu_j^o - RT\,\ln k_i \qquad (7)$$

The summation is over all e elements present in the system, with $\nu_{ij} = 0$ for any element, j, not present in substance i. Furthermore, this expression may be used for substances which are themselves chemical elements by recognizing that for these $\ln k_i = 0$. Using these ideas, the first term in equation (6) may be rewritten.

$$\sum_1^s n_i\mu_i^o = \sum_{i=1}^{s} n_i \left\{ \sum_{j=1}^{e} \nu_{ij}\,\mu_j^o - RT\,\ln k_i \right\}$$

It can be shown that the right hand side here can be arranged as follows.

$$\sum_{1}^{s} n_i \mu_i^o = \sum_{j=1}^{e} \mu_j^o \sum_{i=1}^{s} n_i \nu_{ij} - RT \sum_{i=1}^{s} n_i \ln k_i \qquad (8)$$

Because the elements are neither destroyed nor created by shifts among the n_i, $\sum n_i \nu_{ij} = E_j$, the number of gram atoms of element j originally introduced into the system. Consequently, the first term on the right-hand side of equation (8) is given by

$$\sum_{j=1}^{e} \mu_j^o E_j = G^o$$

where G^o is the absolute Gibbs energy due to the elements, a constant. Therefore, the sum of Gibbs energies for all the substances in standard states is given by the following.

$$\sum_{1}^{s} n_i \mu_i^o = G^o - RT \sum_{1}^{s} n_i \ln k_i \qquad (9)$$

This may be used in (6).

$$G = G^o - RT \sum_{1}^{s} n_i \ln k_i + RT \sum_{1}^{g} n_i \ln (n_i P/n_g) \qquad (10)$$

The right-hand member may be rearranged to give a new function, Γ_G.

$$\Gamma_G = \frac{G-G^\circ}{RT} = \sum_1^g n_i \ln (n_i P/n_g) - \sum_1^s n_i \ln k_i \qquad (11)$$

Now, because G°, R, and T are constants, minimizing Γ_G will minimize G.

Turning at this point to the problem of equilibrium at constant volume and temperature, use is made of the relationship between G and A (ref 1, p 202).

$$A = G - PV \qquad (12)$$

Use of equation (10) gives an expression which will lead to one that is similar to that in (11).

$$A = G^\circ - RT \sum_1^s n_i \ln k_i + RT \sum_1^g n_i \ln (n_i P/n_g) - PV \qquad (13)$$

Assuming that the volume of the condensed phases is negligible compared to that of the gases permits using the (ideal) gas volume for V.

$$PV = n_g RT \qquad (14)$$

At the same time it is possible to replace the variable P.

$$A = G^\circ - RT \sum_1^s n_i \ln k_i + RT \sum_1^g n_i \ln (n_i RT/V) - n_g RT \qquad (15)$$

In view of equation (5) the last term may be put inside the gas summation and the expression rearranged to define the function $= \Gamma_A$.

$$\Gamma_A = \frac{A-G^\circ}{RT} = \sum_1^g n_i [\ln (n_i RT/V)-1] - \sum_1^s n_i \ln k_i \qquad (16)$$

Minimization of Γ_A also minimizes A.

The problem of equilibration has now been shown to require minimization of Γ_G or Γ_A respectively for constant pressure or constant volume. However, these minimizations with respect to the n_i must be carried out subject to constraints: 1. The chemical elements are conserved as previously noted, and, 2. No n_i may be less than zero. The constraints may be expressed as follows.

$$L_j = \sum_1^s n_i \;{}_{ij} - E_j = 0 \qquad j = 1(1)e \qquad (17)$$

$$n_i \geq 0 \qquad\qquad i = 1(1)s \qquad (18)$$

There are e functions, L_j, each of which expresses the conservation of element j such that the E_j equals the number of gram atoms of that element in the system. The E_j are determined from the initial composition. As before, $\;{}_{ij}$ is the subscript for the element j in substance i. Constraint (18) is handled in this development by replacing negative estimates of gaseous constituents by small positive numbers. A negative n_i for a condensed phase assumed to be present indicates the absence of that phase and is retained as an indicator of that fact.

The method of minimization adopted here is the classic one using Lagrangian multipliers, λ_j, [6]. To minimize Γ form the function F by multiplying each of the L_j by λ_j and adding to Γ.

$$F_G = \sum_1^g n_i \ln (n_i P/n_g) - \sum_1^s n_i \ln k_i + \sum_1^e \lambda_j \left[\sum_1^s n_i \nu_{ij} - E_j \right] \quad (19)$$

$$F_A = \sum_1^g n_i \ln (n_i RT/V) - \sum_1^s n_i \ln k_i + \sum_1^e \lambda_j \left[\sum_1^s n_i \nu_{ij} - E_j \right] \quad (20)$$

Minimization of F_G will be treated first in detail. It will be seen later that a few simple changes in the equations will suffice to minimize F_A.

Setting the appropriate partial derivatives of F_G equal to zero results in three sets of equations, one set for the gases, one for the condensed phases, and one for the elements.

$$f_i = \ln n_i - \ln n_g + \ln (P/k_i) + \sum_{j=1}^e \lambda_j \nu_{ij} = 0 \qquad i=1(1)g \quad (21)$$

$$f_i = \ln k_i + \sum_{j=1}^e \lambda_j \nu_{ij} = 0 \qquad i=(g+1)(1)s \quad (22)$$

$$f_i = \sum_{i=1}^s n_i \nu_{ij} - E_j \qquad j=1(1)e \quad (23)$$

It can be seen that there are $s + e$ equations, sufficient to completely determine the s n_i and the e λ_j. The variable n_g is a defined function which is calculated when the n_i have been estimated.

Equations (21) are nonlinear and an iterative procedure, Newton-Raphson [7], is used. In summary, this method iterates from initial estimates of the n_i and the λ_j to a final set which satisfies some stopping criterion. The iterations may be expressed by use of a matrix equation [13].

$$x_{t+1} = x_t - J_t^{-1} f_t \tag{24}$$

Here x and f are column matrices (vectors) representing the unknowns and the functions (21) through (23). Subscript t indicates that the values used are from the t-th trial. J is the Jacobian of the f's, a square matrix with elements equal to the partial derivatives of the functions, f, with respect to the n_i and the λ_j.

There are a variety of types of elements in the Jacobian. Equations (21) yield the following entries.

$$\frac{\partial f_i}{\partial n_i} = \frac{1}{n_i} - \frac{1}{n_g} \qquad\qquad i=1(1)g \tag{25}$$

$$\frac{\partial f_i}{\partial n_k} = -\ 1/n_g \qquad\qquad \begin{cases} i=1(1)g \\ k=1(1)s \\ k \neq i \end{cases} \tag{26}$$

$$\frac{\partial f_i}{\partial \lambda_j} = v_{ij} \qquad\qquad \begin{cases} i=1(1)g \\ j=1(1)e \end{cases} \tag{27}$$

Equations (22) yield the following.

$$\frac{\partial f_i}{\partial n_k} = 0 \qquad\qquad \begin{cases} i=g+1(1)s \\ k=1(1)s \end{cases} \tag{28}$$

$$\frac{\partial f_i}{\partial \lambda_j} = v_{ij} \qquad\qquad \begin{cases} i=g+1(1)s \\ j=1(1)e \end{cases} \tag{29}$$

Equations (23) yield the following.

$$\frac{\partial f_j}{\partial n_i} = \nu_{ij} \qquad \begin{cases} j=1(1)e \\ i=1(1)s \end{cases} \tag{30}$$

$$\frac{\partial f_i}{\partial \lambda_k} = 0 \qquad \begin{cases} j=1(1)e \\ k=1(1)e \end{cases} \tag{31}$$

Expression (25) gives nonzero values to the first g Jacobian elements along the diagonal. Expressions (27) and (29) may be combined.

$$\frac{\partial f_i}{\partial \lambda_j} = \nu_{ij} \qquad \begin{cases} i=1(1)s \\ j=1(1)e \end{cases} \tag{32}$$

Expressions (26), (30), and (32) show that these elements are symmetrically disposed with respect to the diagonal. Since all other elements are zero, J is symmetric. This is an advantage for some methods of calculating the inverse.

These results are easily modified for equilibria at constant volume. The functions (21) are replaced by (33), but (22) and (23) are retained.

$$f_i = \ln n_i + \ln \left(\frac{RT}{V}\right) - \ln k_i + \sum_{j=1}^{e} \lambda_j \nu_{ij} \qquad i=1(1)g \tag{33}$$

Of the Jacobian elements, those in (25) and (26) are changed, replaced by (34) and (35).

$$\frac{\partial f_i}{\partial n_i} = 1/n_i \qquad\qquad i=1(1)g \qquad (34)$$

$$\frac{\partial f_i}{\partial n_k} = 0 \qquad\qquad \begin{cases} i=1(1)g \\ k=1(1)s \\ k \neq i \end{cases} \qquad (35)$$

GENERAL STATEMENT OF THE ALGORITHM

In principle there is no difficulty obtaining equilibrium composi-
tions from the development of the previous section. A problem is defined
by giving values for the constant temperature and the constant pressure
(or volume) and for the composition of the test gas in moles of each
substance.* From the latter the number of gram atoms, E_j, of each
chemical element may be calculated. From the formulae of the substances
the ν_{ij} are also determined. The equilibrium constants of formation may
be obtained from the literature. One needs only initial estimates of
the n_i and the λ_j in order to proceed.

1. Choose initial estimates.

2. Evaluate the functions, equations (21) to (23), using the
    initial estimates.

3. Calculate the elements of the Jacobian, equations (25) to (32).

4. Invert the Jacobian.

5. Calculate the new estimates from equation (24).

6. Check the estimates against the stopping criterion.

7. Depending upon the result of step 6, either stop or repeat
    steps 2 through 6 using the new estimates for evaluation
    purposes.

---

*   In the later section about using the program the instructions ask for
mole fractions or percentages although these data are treated as moles.
Experience with COLGAS has shown that when n_g is much less or much
greater than one, difficulty with over- or underflow may occur.

As straightforward as this procedure is, there are a number of practical points associated with these steps which are worth commenting on. However, the handling of the practical problems depends upon the general aims of the program. Therefore, although some general remarks will be made, it must be understood that the particular procedure adopted in this report is based upon the restricted nature of the problems being solved.

Choosing the Estimates. The program to be developed was to give a "one shot" solution. That is, a single run would produce only a single answer. A different temperature and/or a different pressure (or volume) or test gas composition will require a new run. Consequently, the program has no prior experience to build upon as is used in some programs [8, 14]. It was decided to use the test gas composition as the initial estimates for the substances, and this has turned out to be satisfactory. For each λ_j zero has been a satisfactory initial estimate.

There are two versions of the program in the same listing. The commonly used version has a short printout. Either the short or the long printout is obtained by an appropriate response to the initial query at the terminal. The long version permits the operator to suggest which of the four combinations of condensed species situations is believed to be correct. It then allows input of a set of initial estimates different from that used automatically by the program. These alternatives have been provided so that on occasions of non-convergence an operator may try to redo the iterations with a better starting situation.

Evaluating the Functions. Equations (21) to (23) present no problems
beyond obtaining values for the equilibrium constants of formation for
compounds in the system. (The total number of moles of gases, n_g, is
evaluated anew at each iteration using equation (5)). The equilibrium
constants used in the program, except for liquid water, come from the
JANAF Tables [15] and are discussed in a separate section.

Calculating the Elements of the Jacobian. Examination of equations (25)
to (32) shows that the only elements varying in value from iteration to
iteration are the elements of the upper left 5x5 submatrix. These will
require recalculation during the iteration. All other elements are
constant integers and need not be re-evaluated. However, if the presence
or absence of a condensed phase turns out to be different than assumed,
the presence or absence of the appropriate constant elements must be
adjusted.

Inverting the Jacobian. There is an extensive literature on the inversion
of matrices, particularly symmetric ones [16]. It is tempting to seek
a direct analytical solution with perhaps the possibility of avoiding
some round-off error in the computer. In fact, at constant volume and
for the case where solid carbon is present, but liquid water is not, it
is relatively simple to do this using either an LP or an LDR decomposition
of the Jacobian [17]. There is a minor advantage to this beyond the
possibility of reducing the round-off error. Some of the expressions
for the n_i contain functions of them which may be replaced by the E_j
constants for hydrogen and oxygen. This should improve the accuracy of

the estimates and perhaps reduce the number of required iterations.
However, when the condensed phase situation is reversed, some of the
expressions for the estimates become quite complicated and hardly worth
evaluating directly. Although not essential, it is desirable to handle
all varieties of condensed phase situations in the same way for sim-
plicity of programming. This is particularly true when using the BASIC
programming language because of the one-statement matrix inversion
procedure provided. A direct analytical solution was, therefore, not
used.

Calculating the New Estimates. As is well known, the Newton-Raphson
procedure often overcorrects in the early stages, particularly if the
initial estimates are somewhat far from the mark. This results in
divergence. To avoid this a common procedure is to modify the correct-
ion term in the estimating equation, (24), by a weighting factor, k,
less than unity.

$$x_{t+1} = x_t - k_t \, J_t^{-1} \, f_t \tag{36}$$

In many nonlinear equation problems it is adequate to use $k = 0.5$ in the
early stages and to change it to unity later on. In running this
program it was found that this was not always sufficient. This diffi-
culty was overcome by making k a variable function of t, the number of
the trial. A sinusoidal function of t sets k equal to about 0.01 for t
= 1, to 0.5 for t = 8, and to 1.0 for t = 16. The value of k remains at
unity for any further iterations. This is done only for the gaseous

constituents. Experience with the algorithm has shown that the estimates of the Langrangian multipliers converge easily with k = 1.0 at all stages.

Sometimes new estimates of the gaseous moles become negative. This not only violates the constraint, equation (18), but it cannot be tolerated when evaluating the functions, f_i, which contain $\ln n_i$. Transformations may avoid this problem, $y = n^2$ [4] or $y = \ln n$ [5], but introduce numerous back and forth transformation steps in the algorithm which were thought to be undesirable. The algorithm reported here replaces such numbers with a very small number, originally 1×10^{-7}. It was found that this occasionally led to difficulty when the size of the correction was larger than this figure. A loop of repeated values could result with continually negative estimates for the same n_i leading to a lack of convergence. This difficulty was partially overcome by replacing the 7 in the exponent by a random number distributed uniformly between 7 and 10 inclusive. This choice occasionally leads to a new difficulty with some processors. During the matrix inversion step, usually a Gauss-Jordan routine, the product of the five $(1/n_i - 1/n_g)$ is evaluated. If for a given iteration a number of n_i estimates become negative the n_i product may cause an overflow. This has happened with a compiler for which the exponent of numerical constants is restrained to be within ±38. For a processor with a larger range, say greater than ±55, this difficulty may not arise.

Checking the Estimates for Stopping. The criterion used here for stopping depends upon the magnitude of the unweighted correction to the n_i and the λ_j. The vector c_t is the correction and it comes from (24).

$$c_t = J_t^{-1} f_t \qquad (37)$$

The iterations are considered complete when

$$\frac{c_t}{n_t} < 5 \times 10^{-5} \qquad (38)$$

for all n_i and λ_j. This particular stopping criterion has been criticized, (ref 18, p 520) as not leading necessarily to the same solution as a criterion based upon the derivatives: f_i being sufficiently close to zero. However, because the interest here is in the gas composition the criterion given above is preferable. To assure adequate minimization, the pertinent independent chemical equilibria constants are checked for agreement when calculated from Gibbs energies of formation and from the calculated mole fractions. According to Brinkley [23] there are at most $R = N - C$ reactions for N chemical species and C components. In this discussion $C = 3$ and N equals 5, 6, or 7 depending upon the case. For case IV, all gas, (see below), $N = 5$ and $R = 2$. The reactions chosen were the following.

$$A: \quad CO_2 + H_2 = CO + H_2O$$
$$B: \quad CO + 3H_2 = CH_4 + H_2O$$
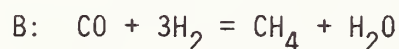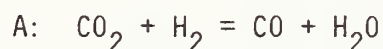
When C(s) is present, reaction C is included, and for liquid water reaction D.

$$C: \quad CO_2 + C(s) = 2CO$$
$$D: \quad H_2O(l) = H_2O(g)$$
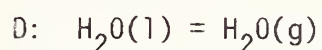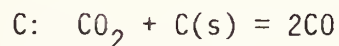
Terminating the Iterations. When the stopping criterion, equation (38) has been satisfied for all n_i and λ_j one set of iterations is complete. The problem may not be solved, however. In order to perform the calculations a choice had to be made among the possible combinations of condensed species situations as shown in Table 2.

Table 2.   Condensed Phase Cases

$H_2O(l)$

		YES	NO
	YES	I - 8	II - 7
C(s)			
	NO	III - 9	IV - 8

Here the yes-no tabulations refer to the presence or absence of the phase at the top or at the left. The Roman numerals are used to identify the cases, and the Arabic numerals show the number of functions, f_i, and correspond to the order of the relevant Jacobian.

Solving the seven-equation system corresponding to case II, say, has assumed the presence of solid carbon and the absence of liquid water. However, this assumption may not be correct. Therefore, after going through steps 1 to 7 and deciding to stop, it is necessary to check the assumption of case II. If liquid water is really present

and/or solid carbon is really absent as suggested by the final n_i, then the appropriate case must be chosen and the iterations redone. There are, therefore, two hierarchies of iterations, one on the n_j and one on the cases. When the final n_i are found to be consistent with the case assumed, the calculation is finally finished. Details of checking case consistency are covered in the section on DETAILS OF THE ALGORITHM.

APPLICATION TO A SIMPLIFIED COAL GASIFICATION SYSTEM

The work shown in this report was undertaken to provide results
with atmospheres used for testing materials to be used in coal gasification
plants. For simplicity the problem was limited to one in which an
initial gas mixture was made from two or more of the following: CH_4, CO,
CO_2, H_2, and H_2O at some temperature, T. The test may be carried out
dynamically in which case constant pressure is assumed. A static test
implies constant volume. Constant pressure will be assumed here. From
what has gone before, extension to constant volume will be obvious.

The first step is to set down the pertinent functions, according to
equations (21) through (23) of the second section, but it is necessary
to decide upon allowable condensed states. Because conditions of test
will not permit the existence of ice, only liquid water need be considered.
The conditions will be above the critical temperatures of the other four
substances so no other solid or liquid phase for these need be considered.
However, decomposition of CH_4 and disproportionation of CO can produce
solid carbon. Consequently, there are two condensed phases to consider,
liquid water and solid carbon. Examination of the simultaneous equations
in the light of this shows that n_c, the number of moles of solid carbon,
appears only once, and that in the equations (23) corresponding to that
element. Allowing indices one through five to refer to the gases in the
order mentioned above

$$n_1 + n_2 + n_3 + n_c - C = 0 \qquad (39)$$

Here C is the E_j for the element carbon. It is unnecessary, therefore, to solve for n_c iteratively. Instead the equation for the constraint due to the element carbon will be deleted. When the other n_i have all been determined, n_c may be calculated from (39). For case II (solid carbon only) the functions to be used are the following.

$$f_1 = \ln n_1 - \ln n_g - \ln k_1 + 4\lambda_h$$

$$f_2 = \ln n_2 - \ln n_g - \ln k_2 + \lambda_o$$

$$f_3 = \ln n_3 - \ln n_g - \ln k_3 + 2\lambda_o$$

$$f_4 = \ln n_4 - \ln n_g - \ln k_4 + 2\lambda_h \tag{40}$$

$$f_5 = \ln n_5 - \ln n_g - \ln k_5 + 2\lambda_h + \lambda_o$$

$$f_6 = 4n_1 + 2n_4 + 2n_5 - h$$

$$f_7 = n_2 + 2n_3 + n_5 - o$$

Here h and o are the E_j for hydrogen and oxygen.

Equations (25) to (31) of the second section lead simply to the Jacobian.

$$
J = \begin{bmatrix}
\dfrac{1}{n_1} - \dfrac{1}{n_g} & 0 & 0 & 0 & 0 & 4 & 0 \\[2.5em]
0 & \dfrac{1}{n_2} - \dfrac{1}{n_g} & 0 & 0 & 0 & 0 & 1 \\[2.5em]
0 & 0 & \dfrac{1}{n_3} - \dfrac{1}{n_g} & 0 & 0 & 0 & 2 \\[2.5em]
0 & 0 & 0 & \dfrac{1}{n_4} - \dfrac{1}{n_g} & 0 & 2 & 0 \\[2.5em]
0 & 0 & 0 & 0 & \dfrac{1}{n_5} - \dfrac{1}{n_g} & 2 & 0 \\[2.5em]
4 & 0 & 0 & 2 & 2 & 0 & 0 \\[2.5em]
0 & 1 & 2 & 0 & 0 & 0 & 0
\end{bmatrix} \quad (41)
$$

The functions of equation (40) and the inverse of the Jacobian (41) are the needed entries for the right hand side of equation (24) of the second section.

The development of case II gives the smallest set of equations to be solved by iteration and give rise to the "basic" Jacobian. This is a 7x7 upper left submatrix common to the cases. Consequently, the elements in it may be defined without regard to case.

The development here was for a particular case. The one with condensation, Case I, with both condensed phases present, follows by adding terms for liquid water to f_6 and f_7: $2n_1$ and n_1 respectively. A function for liquid water is needed.

$$f_8 = 2\lambda_h + \lambda_o = \ln k_\ell \qquad (42)$$

The pertinent Jacobian is equation (41) with another row and column added. The row is given by j_8.

$$j_8 = \{0,0,0,0,0,2,1,0\} \qquad (43)$$

The column is the transpose of this.

Case III, with liquid water but no solid carbon, requires f_8 and n_w but has no n_c. Because there is no n_c equation (39) becomes

$$f_9 = n_1 + n_2 + n_3 - C \qquad (44)$$

This function must be included as well as a λ_c. A new row and column are added to the Jacobian consisting of ones in the first three elements and zeros elsewhere. This is the largest matrix and has nine rows and columns.

Case IV, with neither liquid water nor solid carbon, is derivable from Case III by elimination of the eighth row and column. These correspond to liquid water and λ_ℓ. Also the function, f_8, is deleted. The problem of determining equilibrium compositions in the system is then resolved to choosing the appropriate form of the Jacobian, (41), depending upon the case. Deciding the appropriate case for any given problem without any prior knowledge is difficult. As was seen in the previous section, the algorithm given here assumes a starting case and checks the results for consistency with this assumption.

THERMODYNAMIC DATA

For the five gases, CH_4, CO, CO_2, H_2, H_2O, the tabular data of the JANAF Tables [15] between 300 and 1400 K were fitted by least squares to equations of the form

$$\ln k_i = a_1 + a_2 \ln T + \sum_1^m a_{i+2} T^i \qquad (45)$$

Here, as stated earlier, k_i is the equilibrium constant of formation of the i-th compound in its standard state and from its elements in their standard states. The constant for hydrogen is, of course, unity so that the corresponding $\ln k_i$ equals zero. The value of m was determined by trials with m = 2(1)5. The smallest $m \geq 2$ so that the standard error of the residuals $\leq .001$ was chosen. The form of this equation is similar to that of Barron, Porter, and Hammond [19] but the latter authors used a fixed highest power equal to five. The least squares coefficients were determined with the computer language OMNITAB [20] which has an accurate least squares routine [21].

Liquid water is not included in the JANAF Tables, so resort was had to combining the JANAF data for gaseous H_2O, k_5, with the vapor pressure, p_s.

$$\ln k_\ell = \ln k_5 - \ln p_s \qquad (46)$$

For the vapor pressure data, Schmidt's tabular values [24] were used and fitted by least squares to an equation of the following form.

$$\ln p_s = b_1 + b_2/T + \sum_{i=1}^{m} b_{i+2} T^i \qquad (47)$$

In this case the data were sufficiently detailed that a tighter criterion could be used for m. The smallest m was chosen for which the maximum residual ≤ 0.0005. The results, $\ln k_i$ for the gases and $\ln p_s$ for $H_2O(\ell)$ are shown in the table.

Table 3. Empirical Coefficients for the $\ln k_i$ and $\ln p_s$

$\ln k_i$	a_1	a_2	$a_3 \times 10^3$	$a_4 \times 10^6$	$a_5 \times 10^9$	$a_6 \times 10^{13}$
CH_4	8212.35	-0.816063	-10.0801	7.73804	-3.06981	5.08552
CO	13632.3	1.8055	- 2.3936	0.372836	---	---
CO_2	47326.7	0.0777872	- 0.280706	0.0348747	---	---
$H_2O(g)$	28786.6	-0.697311	- 1.45957	0.83769	-0.180286	---
	b_1	b_2	b_3	$b_4 \times 10^4$	$b_5 \times 10^7$	$b_6 \times 10^{10}$
$\ln p_s$	55.5049	-9430.74	-0.159684	3.07499	-3.0549	1.24325

The maximum residual for any of the nonzero $\ln k_i$ to be used is 0.00186 for $\ln p_s$. Program trials with $\ln k$ differing by 0.01 showed absolute values of changes in the computed $n_1 \leq 0.0001$. The accuracy of the coefficients in the table is quite adequate for the purpose.

DETAILED ALGORITHM

Master Flowchart. The details of the algorithm will be described in terms of flowcharts for some sections and with an overall chart showing the relationship of the pieces. It will be noticed that although some sections of the program could be subroutines, they are not. There are no "gosub" and "return" statements. There is no advantage to having formal subroutines here. Replacement of a section is no more difficult than replacing a subroutine because BASIC statements must all have line numbers which must be adjusted in either case. Furthermore, because one cannot fruitfully use dummy variables, one of the advantages of a FORTRAN type subroutine is lost.

The master flowchart is shown as Figure 1. Most of the items are self-explanatory, however, some remarks about others will be useful.

The first major branch point reflects the impossibility of $H_2O(1)$ existing above its critical temperature, 647.3 K, and below that at total pressures less than its vapor pressure. This is a useful distinction because it rules out two of the four cases, I and III. The choice of II and IV as starting cases for the respective branches resulted from the experience that these led more often to convergence of the first set of iterations. A longer experience may suggest alternate choices. Note that the variable c_1 is assigned the value of the case number assumed at the start of a set of iterations. This is required for the case-consistency checking section.

The Newton-Raphson iterations follow in either case. These will be treated later by a separate flowchart. Upon successful convergence of
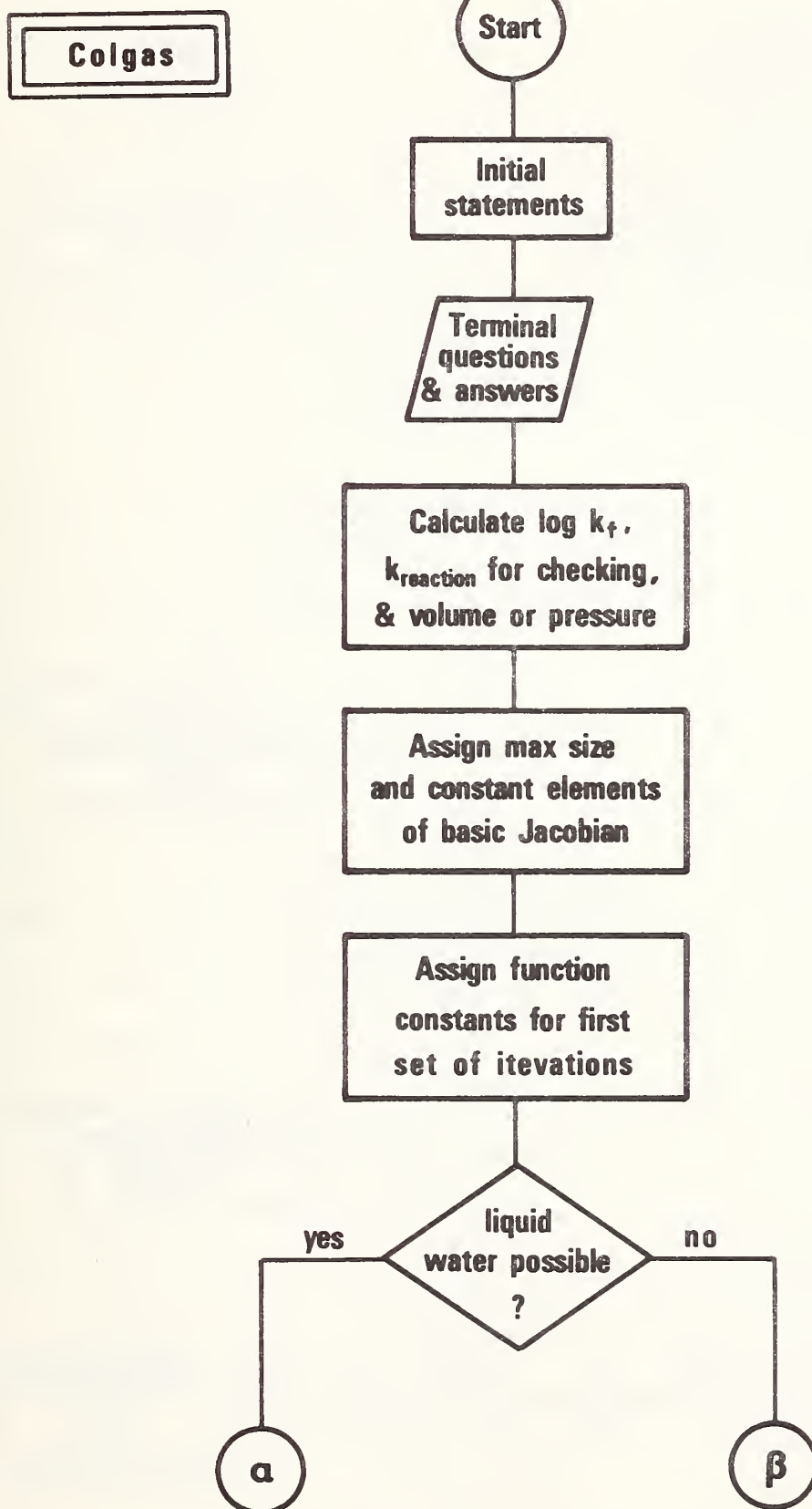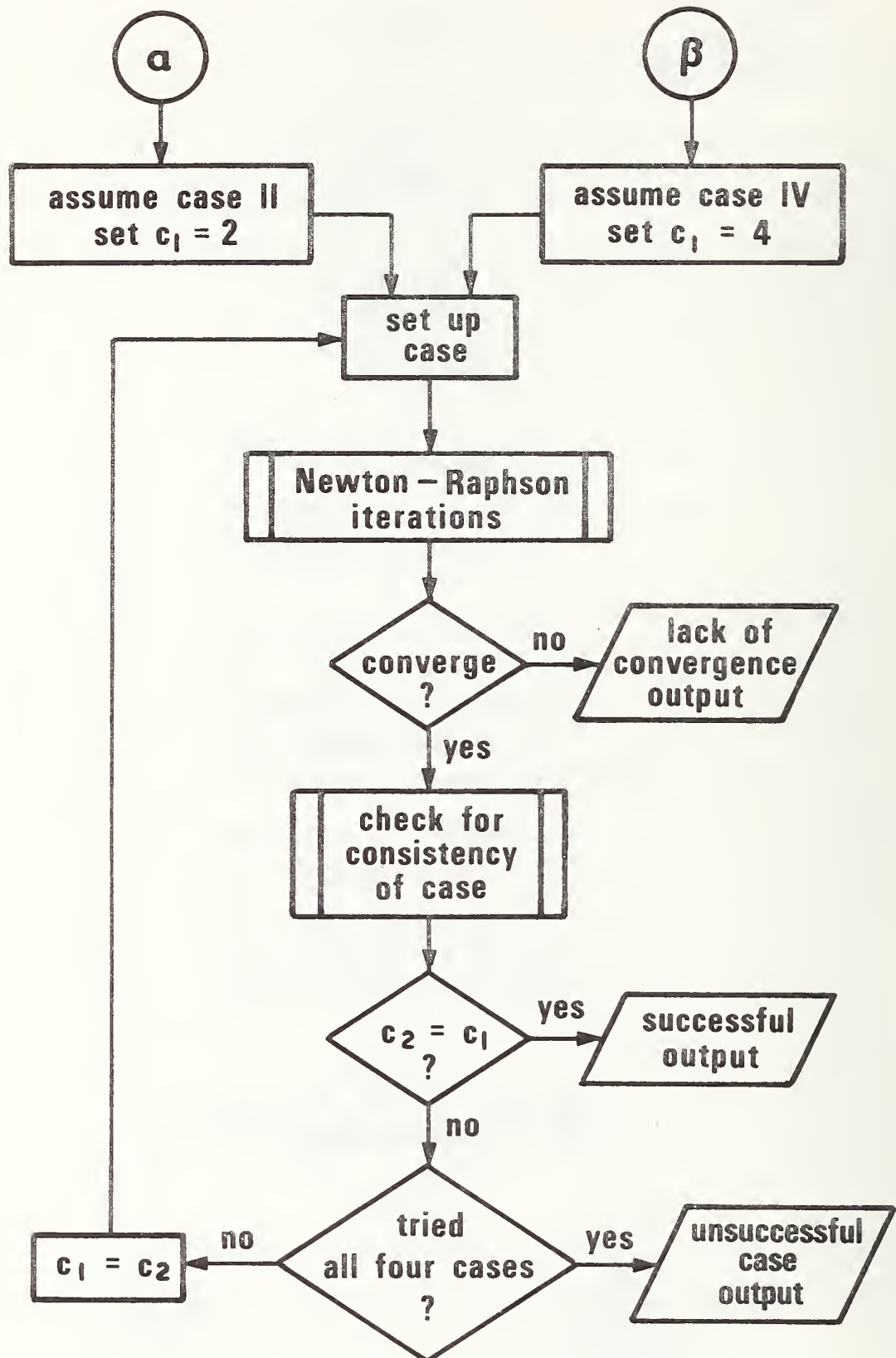
Figure 1a

Figure 1b

the iterations, the next step is to check the case suggested by the results. Upon unsuccessful convergence, the "lack-of-convergence output" results. The latter not only states lack of convergence but also gives the case number that had been assumed and the last set of iterated results. These outputs are useful if it is desired to try again with a different set of initial estimates.

The case-checking section will be presented in a detailed flowchart. Essentially it computes the case number, c_2, suggested by the success-fully converged results and compares this with c_1. If they are equal then a "successful output" results which gives the equilibrium gas composition, quantities of liquid water and/or solid carbon if either or both are present, and the changed volume (or pressure). If c_2 does not equal c_1 then a counter is compared with the number four. If four cases have been tried then an "unsuccessful output" is produced stating this fact. This kind of result has not yet appeared in practice (April 11, 1978), however, the possibility has been allowed for. If four cases have not yet been tried c_1 is set equal to c_2 and the program returns to that case for another set of iterations.

Newton-Raphson Iterations. The flowchart for this section appears in Figure 2. The iteration counter, t_1, allows up to 30 trials. It has been the usual experience with this program that if convergence has not been reached in 30 iterations, it will not be reached by going beyond this point. Commonly, convergence is attained with between 10 and 20 trials. It would take less, but, for the cautiously slow start enforced by the weighting factor, k.
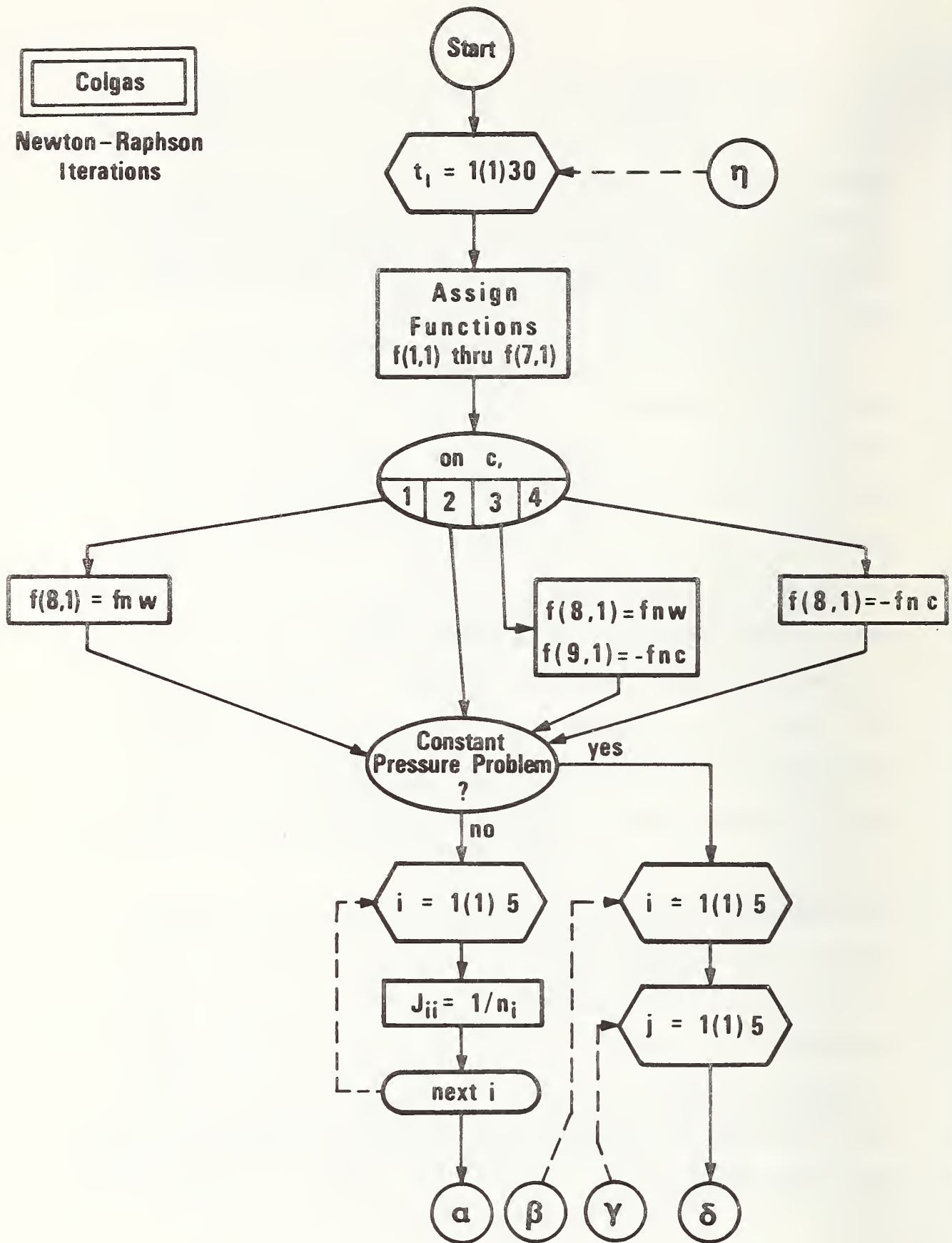
Figure 2a

Figure 2b

Figure 2c

$$k_4 = x_2 \, x_5 \, / \, x_3 \, x_4$$
$$k_5 = x_1 \, x_5 \, / \, x_2 \, x_4{}^3 \, p^2$$
$$k_6 = x_2^2 \, p \, / \, x_3$$
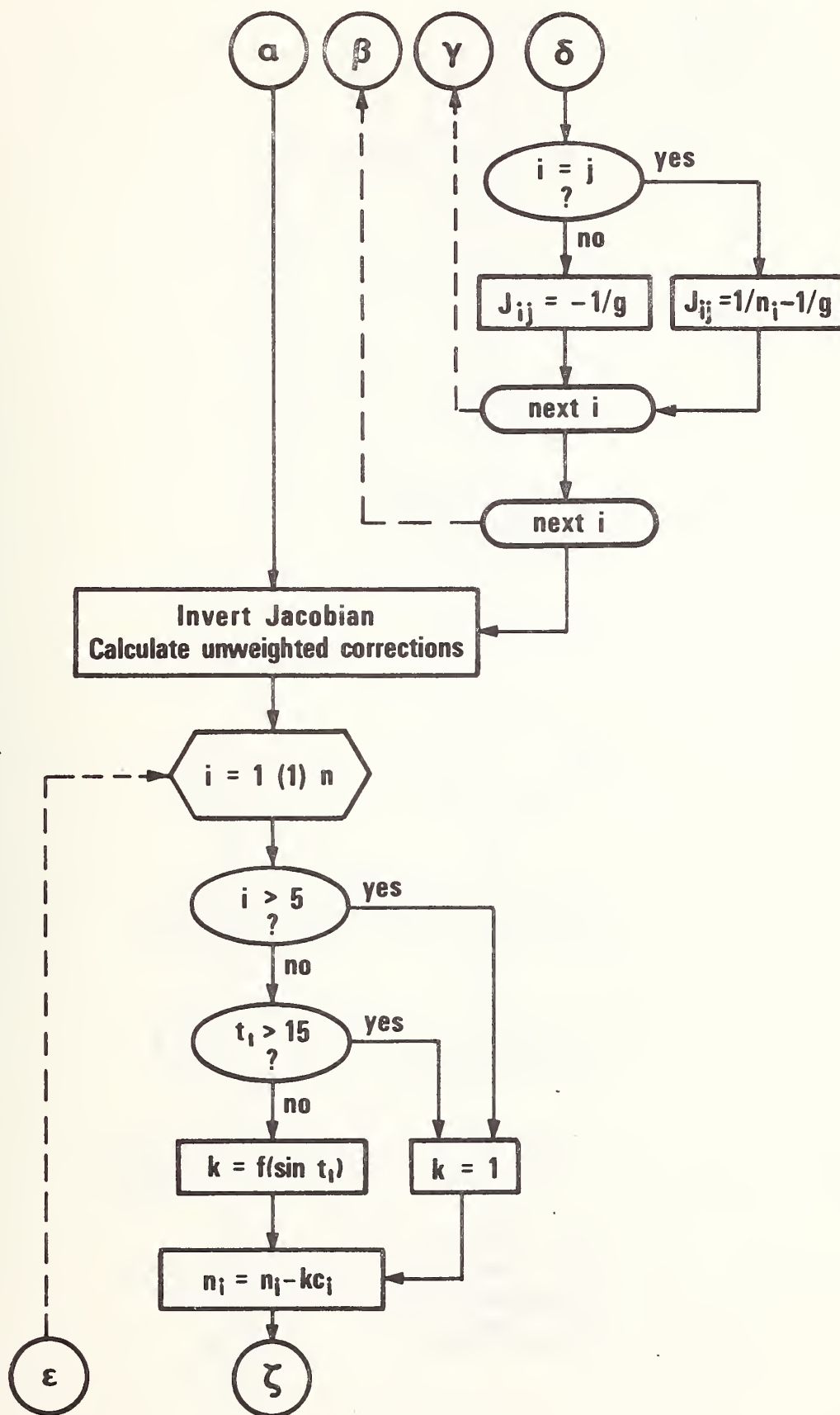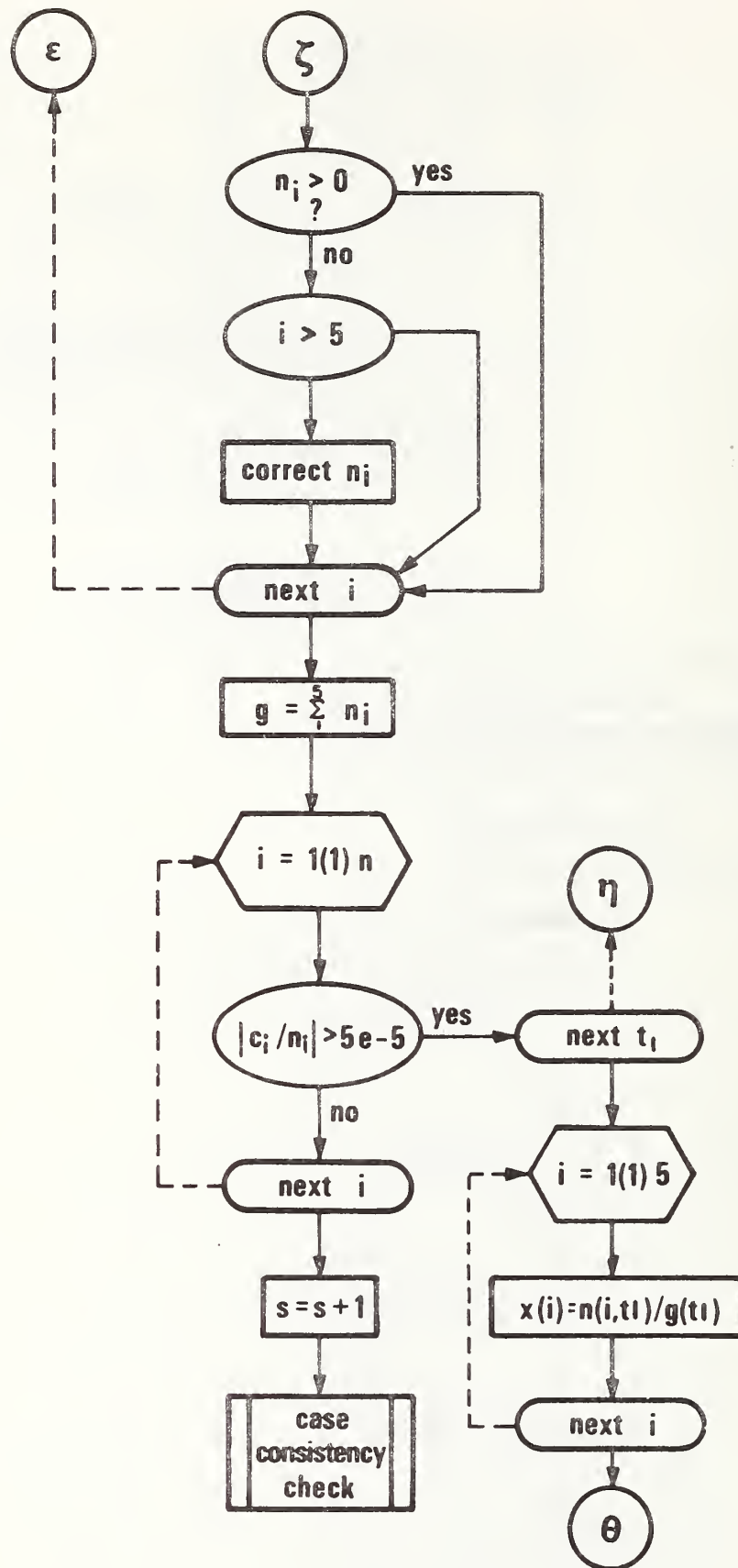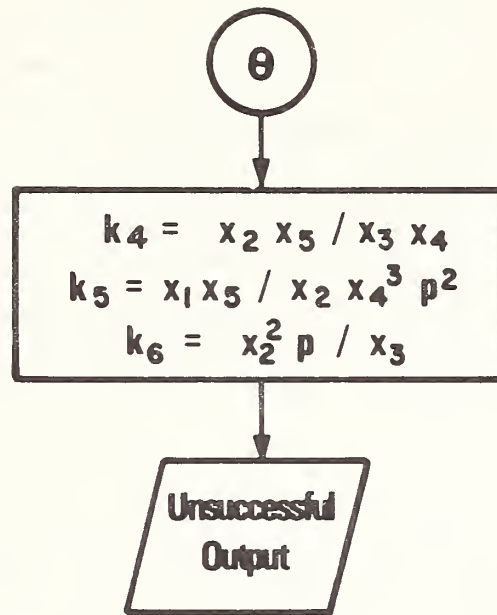
Figure 2d

Initially, the seven functions which, with slight variations, are common to all four cases, are evaluated using the previously determined $\dot{n}_i$. The variations required for the different cases are achieved by using two constant multipliers b and d, which are set independently equal to zero or unity depending upon the case. A third constant, e, is the subscript for λ_c, the Lagrangian multiplier for the element carbon in cases III and IV when solid carbon is not present. Since λ_c is always last in these cases, e is set equal to n, the size of the appropriate Jacobian. Next, via an "on c_1" statement, the appropriate remaining functions for cases I, III, and IV are assigned. This is accomplished with the user-defined BASIC functions fnw and fnc.

Following the assignment of the functions, the elements of the upper left 5x5 submatrix of the Jacobian are evaluated. As stated earlier, these depend upon whether the problem is for constant pressure or constant volume.

Once evaluated, the Jacobian is inverted and unweighted corrections calculated. The next part of the diagram introduces the weight factor, k, which is applied only to the five gases and then up to only trial 15. Following the correction of all n_i, the number of moles of gas is calculated.

The next operation is a loop testing all n_i against the stopping criterion. If successful for all, s, the counter of iteration sets is incremented by one and the calculation proceeds to testing the condensed phase case found against the one assumed.

Case-Consistency Check. In Figure 3, this section begins by calculating mole fractions for the five gases. These are used to calculate equilibrium constants for the three independent reactions and the partial pressure of water. As stated earlier these are used to check the final solution found by minimization of the reduced relative Planck function. (See the subsection on Checking the Estimates for Stopping.) Although only k_6, for the disproportionation reaction, is used in this section they are all calculated together.

The determination of the case found by the converged iterations depends upon the case that was assumed. If that was case III or IV then the conservation of the element carbon was enforced. In these circumstances, by comparing the equilibrium constant for disproportionation (chemical equation C) calculated with the mole fractions with that calculated from the Gibbs energies of formation the need for solid carbon can be determined. On the other hand, if carbon is assumed present then the defined function fnc indicates whether its presence has been verified.

For liquid water cases I and III go together by assuming its presence. For those cases the sign of n_1 is the indicator. For cases II and IV, n_1 is not calculated, therefore, the partial pressure of water is checked against the vapor pressure.

The value of c_2 is built up by an initial assignment and addition as the program works its way through this section. Upon reaching its final value, c_2 is compared with c_1 as stated earlier. Before returning to the appropriate case, if that is necessary, c_1 is set equal to c_2.
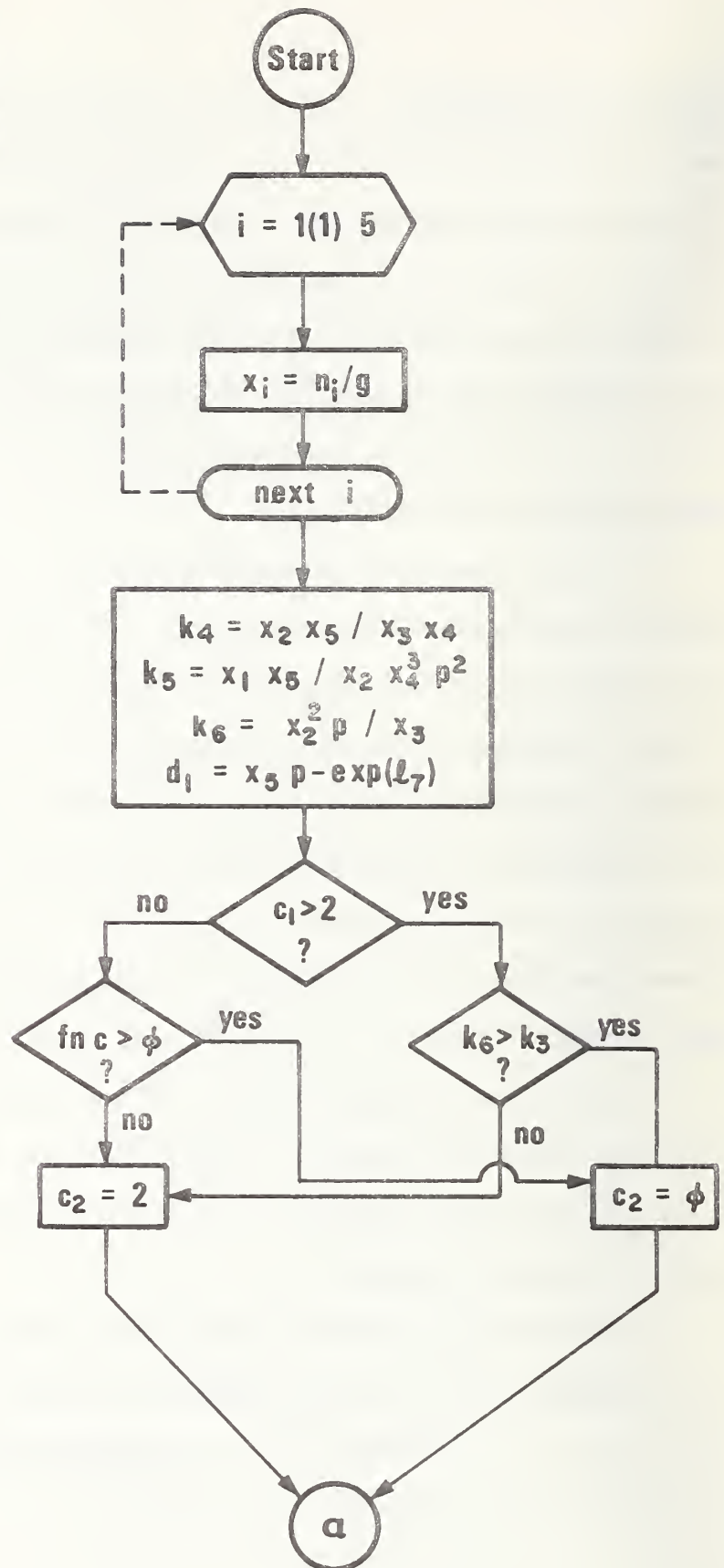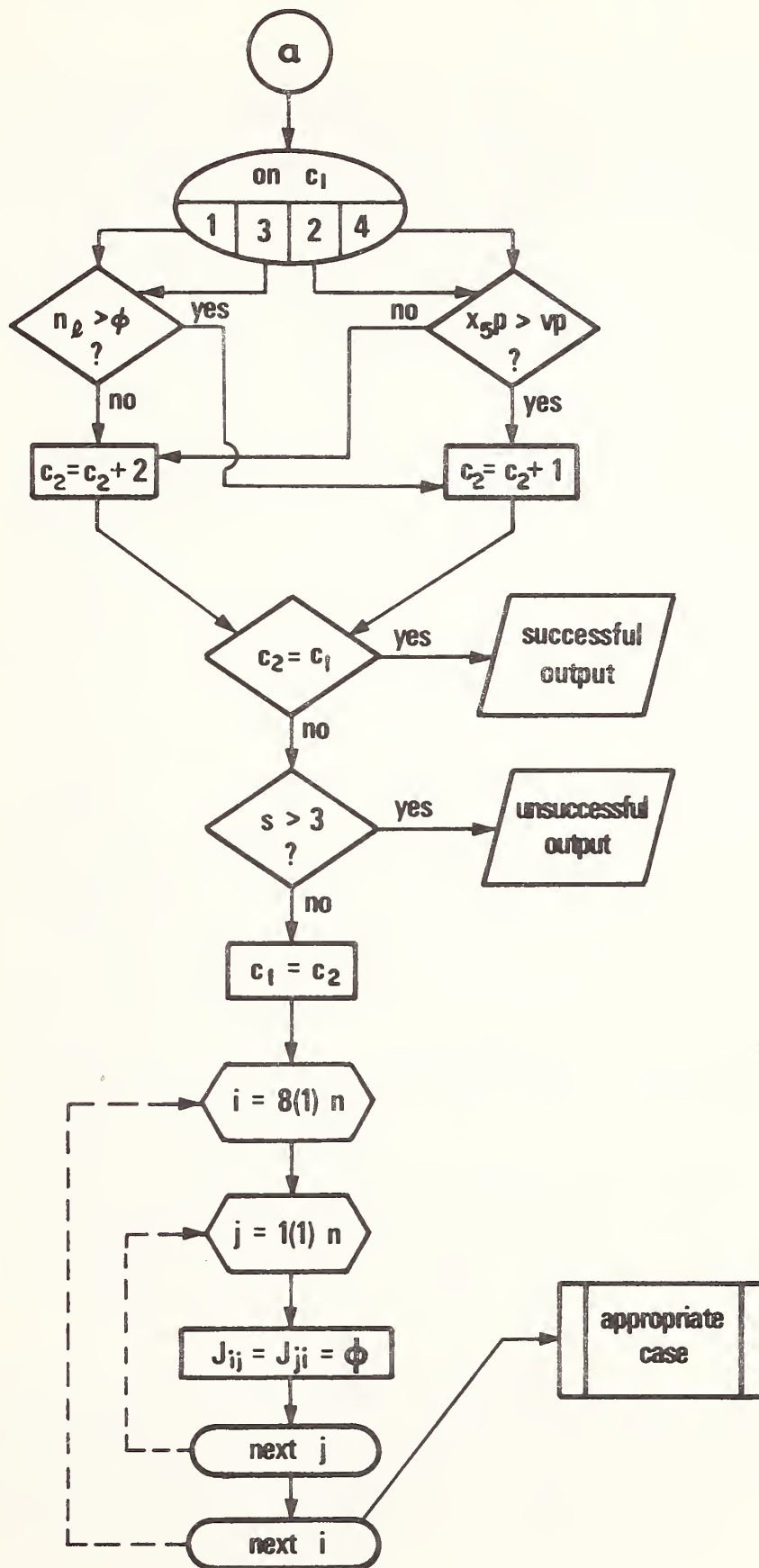
42

Colgas

Case – consistency
check

Figure 3a

Figure 3b

Also it is necessary to clear the eigth and ninth rows and columns of the Jacobian preparatory to inserting the appropriate values for the next case.

DISCUSSION OF THE LISTING

Appendix 1 gives the list of symbols for the mathematical development in the text and Appendix 2 is for the source program. Wherever possible, the same variable symbol has been used in the text and in the computer program. To avoid cluttering the text, variables used there often have fewer subscripts than the corresponding symbols of the program.

The listing, which is Appendix 3, is given in the full ASCII character set. As stated earlier, it is dependent upon the BASIC compiler used by the Computer Sciences Corporation.* At this writing (April 11, 1978) there is no standard for the BASIC language as there is for FORTRAN [22]. On the other hand almost all BASIC compilers provide reasonably useful diagnostics and internal editing commands so that translation to another compiler should not be a great chore.

Use of the full ASCII set permits use of upper and lower case letters. This has been used to differentiate vectors and matrices. The former, even when the unity dimension is explicitly indicated, are given by lower case letters, as are unsubscripted variables. Matrices are in upper case as are elements of matrices.

Sections are separated by remark statements with leading single quote characters. Some statements are amplified by remarks after a

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* A particular commerical source is identified in this paper in order to explain the procedure adquately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the service is necessarily the best for the purpose.

single quote character. Loops have been doubly indented in order to catch the eye, and inner, nested loops are each indented again. The listing is packed, i.e., blanks have been omitted in the program statements except for explanatory matter and output text. The experienced BASIC programmer reads this with ease, and a some storage space is saved.

INFORMATION FOR USING THE PROGRAM

Input. After signing on at the terminal the program COLGAS is LOADed and RUN. The following queries will result.

The program first asks whether the problem is to be for constant pressure or volume and whether a short or long printout is desired. The long printout is generally only used when attempting to rerun a non-converging problem. The answer to these joined questions is therefore generally "p,s" or "v,s". For the long printout "s" is replaced by "1".

The next question concerns the temperature and pressure (or volume). The answers, again separated by a comma, are in kelvins and atmospheres (or liters). Alternatively, degrees Celsius and/or megapascals may be used if the values are preceded by an asterisk without separation by commas or blanks.

The concentrations of the assumed gases are requested next, and the response is to be in mole or volume (decimal) fractions. The answers are typed in the order CH_4, CO, CO_2, H_2, H_2O with separating commas. If any of these are not present, zeros must be entered in the appropriate places. If the input concentrations do not satisfy certain requirements, the operator will be requested to try again.

The computer program does not consider problems in which all three elements, C, H, and O are not present, i.e., if $CH_4 + H_2$, $H_2 + H_2O$, or $CO + CO_2$ are used as starting mixtures. In the first two cases only decomposition of the compounds can occur; in the third only dispro-portionation. (It is assumed that the decomposition of H_2 and CO are negligible.) Such equilibria are calculated by hand directly and

without iteration. It is also true that a mixture of CO_2 and H_2O does not undergo appreciable reaction.

At this stage, input for the short output is complete. If the long output was chosen the following extra input is requested.

The opportunity to choose the starting case will be next presented. The response is "yes" or "no". If "yes" is typed, the (Arabic) number of the preferred case is requested.

Finally, the operator is to decide if a preferred set of initial estimates is to be used; "yes" or "no". If "yes", the preferred values are requested and these are typed in the same fashion as the assumed gas concentrations. Estimates for only the five gases are to be entered. This is the end of the operator input.

Output. All input data are reprinted as an echo check. After the input gas concentrations have been echoed, the unchosen quantity, volume or pressure, is given. Because the number of moles of gas almost always changes in the final equilibrium, all extensive quantities are quoted on the basis of the number of moles of the assumed gas. Although pressure is not an extensive quantity it too can only be quoted on this basis when a constant volume problem is calculated because the number of moles of gas in the input volume has not been requested.

A long printout gives at this point the assumed case and the results of each iteration until the program terminates successfully or unsuccessfully. In the latter situation a statement about unsuccessful convergence is followed by the last set of estimates. In any case the mole fractions

are next and these are followed by the number of moles of gas and the new volume (or pressure).

If liquid water or solid carbon are produced a pertinent statement is made at this point. If the temperature is above the critical value for water, such a statement is made next.

Normally, that is the end of the printout. However, if the run was unsuccessful the independent equilibria will not have been satisfied and statements to this effect will be the last output.

THE PHASE RULE

For the restricted sets of problems considered here, the phase rule
is simple to apply. It is given by equation (48).

$$F = C - P + 2 \qquad\qquad (48)$$

The number of degrees of freedom, F, is the number of independent
choices of variables possible with a given system which has P phases and
C components. In order to use the traditional symbols for the phase
rule, P has been used here, although it has been used before. Because
this applies only to this section, confusion should not result. There
are three possible phases, gas, liquid water, and solid carbon. The
number of components in these problems is equal to the number of chemical
elements, three. This simplifies equation (48).

$$F = 5 - P \qquad\qquad (49)$$

In case IV (see the section on General Statement of the Algorithm)
there is only the gas phase, and there must be four variables available
for choice. Since two are assumed to be temperature and pressure (or
volume), there are two left for concentrations. Thus, if a triangular
diagram is used for the concentrations of the elements carbon, hydrogen,
and oxygen, the possible elemental concentrations would be represented
by an area. See Figure 4. If two atomic compositions are chosen, the
third is fixed by the requirement that the percentages add to 100.

On the other hand for an equilibrium that has either solid carbon
or liquid water (but not both) present, there is only one degree of

PHASE DIAGRAM
C, H, O

700 K
1 atm.

C

CO

CO_2

C(s) & GAS

H_2O

GAS ONLY

CH_4

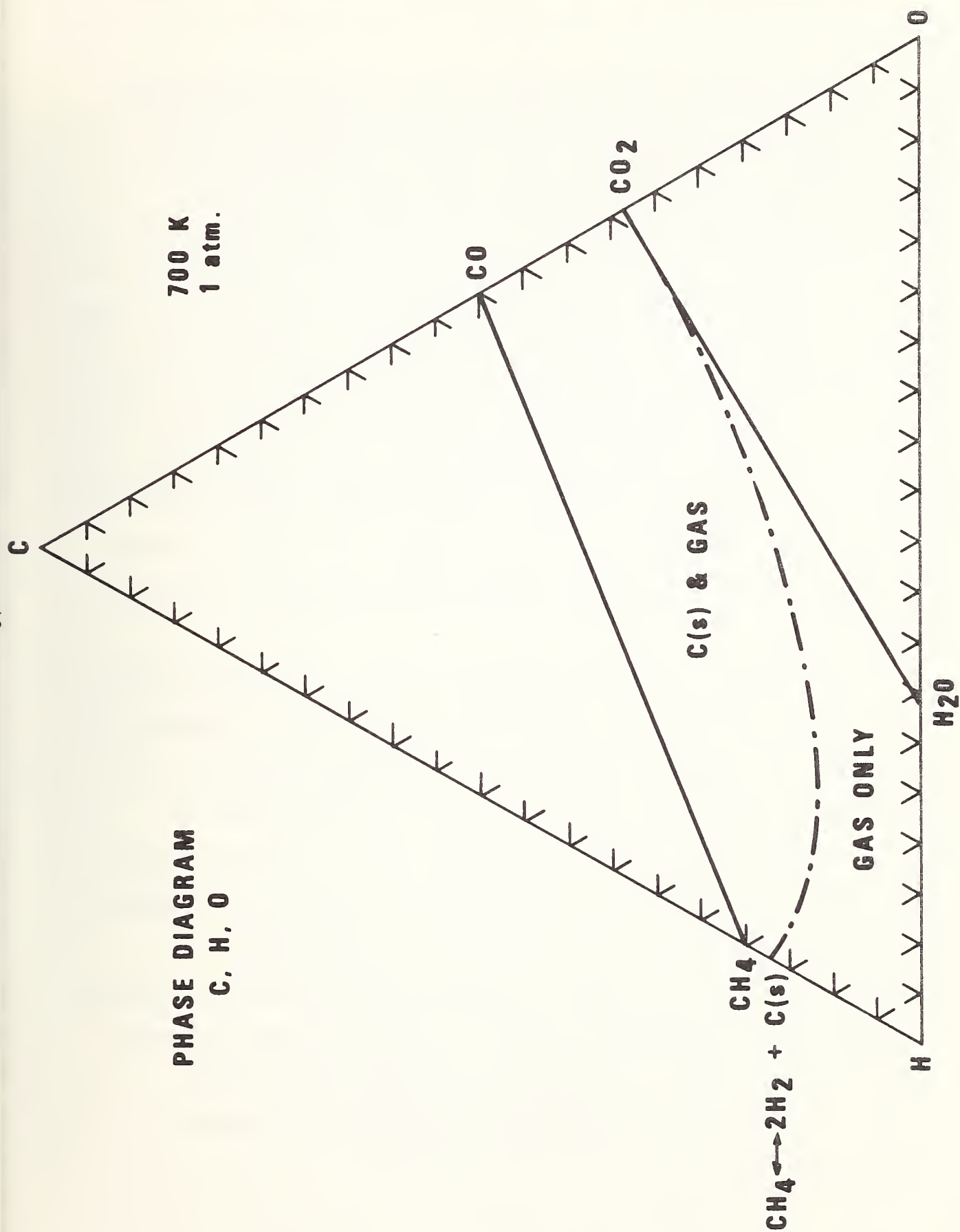$CH_4 \longleftrightarrow 2H_2 + C(s)$

H

O

Figure 4

freedom, and this must be represented by a line. Choosing the percentage for just one element fixes both of the others if one condensed phase is present. Also, because the condensed phase always has a fixed composition, the variable composition refers to the gas phase. Referring to Figure 3, the curved line shows the gas compositions in equilibrium with solid carbon at 700 kelvins and 1 atmosphere. The curve has been drawn by connecting points calculated with COLGAS which turned out to be case II. If a gas mixture contains 15 atomic percent carbon and is in equilibrium with solid carbon the the gas could contain also about 48 atomic percent hydrogen and 37 percent oxygen. Alternatively, it could contain 81 percent hydrogen and 4 percent oxygen. The two possibilities are at the intersections of the 15 percent carbon line with the calculated curve.

A valuable use of the phase diagram in Figure 4 is to show potential carbon precipitation for an assumed test gas mixture. One needs merely to calculate the elemental composition from the compound composition and locate that point on the diagram. If it falls in the area above the curve, carbon will precipitate. Furthermore, extending the line through the apex (for c = 100%) and the point to the curve will give the elemental, but, not the compound composition of the gas in equilibrium with the carbon. It should be noted that gas mixtures made from the five postulated substances will have elemental compositions within the region bounded by connecting the compositions of all of the substances with straight lines. The lines should connect CH_4, CO, CO_2, H_2O, H_2, and return to CH_4 in that order.

Figure 4 represented a situation above the critical temperature of water. Figure 5 illustrates the situation for 500K and 50 atmospheres. The diagram is rather more complicated. Although not always indicated, a gas phase is present for all regions of the diagram. There are two invariant points and two regions within which gas compositions will change to one or the other resulting in condensed water and carbon. There are two regions within which the change will result in carbon only, and two more from which only water will condense. Note the two small regions within which no condensation will occur, although five gaseous substances may change their relative amounts.

PARTIAL
PHASE DIAGRAM
C. H. O

500 K
50 atm.

54
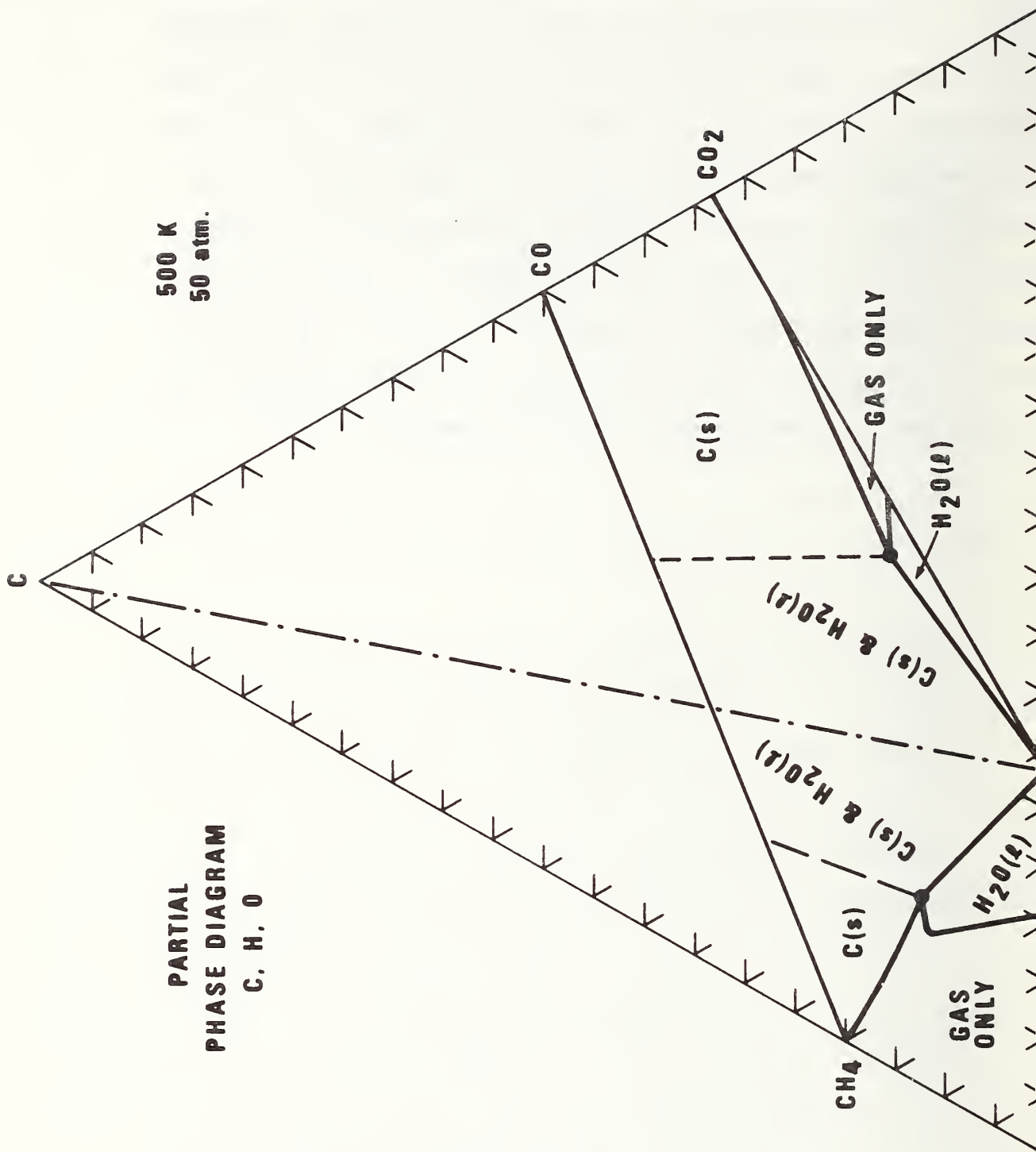
EXAMPLES

Examples A through D are representative of cases I through IV and are successful short printout results. Example B, for 700K and 1 atmosphere, corresponds to the conditions for the phase diagram of Figure 3. The original elemental proportions are .6:1.6:.8 and the atomic fractions are .2, .533, and .267. The line extended from the apex through this point on the diagram intersects the curve for solid carbon at approximately .13, .58, and .29. The equilibrium mole fractions for the five substances give for the atomic fractions in the order C, H, O: .1288, .5809, and .2904.

Example E is for a problem which did not converge during the short-printout run. The last set of estimates suggests that the difficulty involved the amounts of CO and CO_2 which appeared to be continually going negative. Often in a situation of this kind it was found that the initial estimates for such substances were not small enough. Consequently, for the long printout run, example F, initial estimates were chosen equal to the last set from the short run except for the CO and CO_2 which were made smaller.

Example A

colgas 13:14 04/07/78

Is this a constant pressure (p), or a constant volume (v) problem, and do you want a short (s) or a long (l) printout?p,s

What are the temperature (kelvins) and pressure (atmospheres)?500,100
Temperature = 500 K = 226.85 C
Pressure = 100 atm = 10.1325 MPa

What are the assumed concentrations in mole fractions of the gases in the order: CH_4, CO, CO_2, H_2, and H_2O?.1,.1,.1,.4,.3
.1 .1 .1 .4 .3

The initial volume = .410284 liters per mole of original gas

Gas contains C, H, and O atoms in the proportions .3 , 1.8 , and .6

Equilibrium mole fractions in the order CH_4, CO, CO_2, H_2, H_2O are:
.7301   .0000   .0077   .0016   .2606

The number of moles of gas = .2074 per mole of original gas
The volume = 8.50928e-2 liters per mole of original gas

Solid carbon is present in the amount of .1470 moles per mole of original gas
Liquid water is present in the amount of .5428 mole per moles of original gas
now at end

Example B

colgas   13:16   04/07/78

Is this a constant pressure (p), or a constant volume (v) problem, and
do you want a short (s) or a long (l) printout?p,s

What are the temperature (kelvins) and pressure (atmospheres)?700,1

Temperature = 700 K = 426.85 C
Pressure = 1 atm = .101325 MPa

What are the assumed concentrations in mole fractions of the gases in
the order: CH_4, CO, CO_2, H_2, and H_2O?.2,.2,.2,.2,.2
 .2 .2 .2 .2 .2

The initial volume = 57.4398 liters per mole of original gas

Gas contains C, H, and O atoms in the proportions .6 , 1.6 , and .8

Equilibrium mole fractions in the order CH_4, CO, CO_2, H_2, H_2O are: .1693
.0076   .2344   .1376   .4511

The number of moles of gas = .8626 per mole of original gas
The volume = 49.5486 liters per mole of original gas

Solid carbon is present in the amount of .2452 moles per mole of
original gas

Above the critical temperature for water
now at end

Example C

colgas   13:18   04/07/78

Is this a constant pressure (p), or a constant volume (v) problem, and do you want a short (s) or a long (l) printout?p,s

What are the temperature (kelvins) and pressure (atmospheres)?500,50
Temperature = 500 K = 226.85 C
Pressure = 50 atm = 5.06625 MPa

What are the assumed concentrations in mole fractions of the gases in the order: CH_4, CO, CO_2, H_2, and H_2O?.05,.1,.05,.5,.3
 .05 .1 .05 .5 .3

The initial volume = .820569 liters per mole of original gas

Gas contains C, H, and O atoms in the proportions .2 , 1.8 , and .5

Equilibrium mole fractions in the order CH_4, CO, CO_2, H_2, H_2O are: .4730
 .0000   .0012   .0047   .5211

The number of moles of gas = .4218 per mole of original gas
The volume = .34611 liters per mole of original gas.

Liquid water is present in the amount of .2792 moles per mole of original gas
now at end

Example D

colgas   14:22   05/03/78

Is this a constant pressure (p), or a constant volume (v) problem, and
do you want a short (s) or a long (l) printout?v,s

What are the temperature (kelvins) and volume (liters)?1255,1.514
Temperature = 1255 K = 981.85 C
Volume = 1.514 liters

What are the assumed concentrations in mole fractions of the gases in
the order: CH_4, CO, CO_2, H_2, and H_2O?.05,.18,.12,.25,.4
 .05 .18 .12 .25 .4

The initial pressure = 68.0194 atm per mole of original gas

Gas contains C, H, and O atoms in the proportions .35 , 1.5 , and .82

Equilibrium mole fractions in the order CH_4, CO, CO_2, H_2, H_2O are:
.0169   .1902   .1218   .3342   .3368

The number of moles of gas = 1.0640 per mole of original gas
The pressure = 72.37 atm = 7.33289 MPa per mole of original gas

Above the critical temperature for water
now at end

Example E

colgas   14:14   05/03/78

Is this a constant pressure (p), or a constant volume (v) problem, and
do you want a short (s) or a long (l) printout?p,s

What are the temperature (kelvins) and pressure (atmospheres)?500,50
Temperature = 500 K = 226.85 C
Pressure = 50 atm = 5.06625 MPa

What are the assumed concentrations in mole fractions of the gases in
the order: CH_4, CO, CO_2, H_2, and H_2O?.12,0,.01,.75,.12
 .12 0 .01 .75 .12

The initial volume = .820569 liters per mole of original gas

Gas contains C, H, and O atoms in the proportions .13 , 2.22 , and .14
30 iterations did not converge!

The results at this stage are as follows
Case IV
The last set of estimates is, moles and multipliers:
 .13 1.e-9 1.e-9 .71 .14 1.79487 54.3204 13.1832

Equilibrium mole fractions in the order CH_4, CO, CO_2, H_2, H_2O are: .1327
.0000   .0000   .7245   .1429

The number of moles of gas = .9800 per mole of original gas
The volume = .804157 liters per mole of original gas

Equilibrium constants do not check out
First equilibrium constant = 7.24886e-3 vs. .197184
Second equilibrium constant = 1.20341e+10 vs. 19534.9
Third equilibrium constant = 1.61777e-9 vs. 5.10204e-8

now at end

Example F   -

colgas   14:16   05/03/78

Is this a constant pressure (p), or a constant volume (v) problem, and
do you want a short (s) or a long (l) printout?p,l

What are the temperature (kelvins) and pressure (atmospheres)?500,50
Temperature = 500 K = 226.85 C
Pressure = 50 atm = 5.06625 MPa

What are the assumed concentrations in mole fractions of the gases in
the order: CH_4, CO, CO_2, H_2, and H_2O?.12,0,.01,.75,.12
 .12 0 .01 .75 .12

The initial volume = .820569 liters per mole of original gas

Gas contains C, H, and O atoms in the proportions .13 , 2.22 , and .14
Do you want to choose the starting case?no
no

Do you want to provide your own initial estimates?yes
yes

What are they in the same order as above? .13 1.e-15 1.e-14 .71
.14

 0 .13 1.e-15 1.e-14 .71 .14
 0 0 0

Case IV

1	.13	1.00465e-15	1.01427e-14	.71	.14	-1.79487	54.3204	13.1832
2	.13	1.023e-15	1.071053-14	.71	.14	-1.79487	54.3204	13.1832
3	.13	1.0628e-15	1.1989e-14	.71	.14	-1.79487	54.3204	13.1832
4	.13	1.12872e-15	1.4278e-14	.71	.14	-1.79487	54.3204	13.1832
5	.13	1.21986e-15	1.78602e-14	.71	.14	-1.79487	54.3204	13.1832
6	.13	1.32744e-15	2.28501e-14	.71	.14	-1.79487	54.3204	13.1832
7	.13	1.43493e-15	2.89084e-14	.71	.14	-1.79487	54.3204	13.1832
8	.13	1.52342e-15	3.50313e-14	.71	.14	-1.79487	54.3204	13.1832
9	.13	1.58122e-15	3.98772e-14	.71	.14	-1.79487	54.3204	13.1832
10	.13	1.60992e-15	4.26874e-14	.71	.14	-1.79487	54.3204	13.1832
11	.13	1.62027e-15	4.38108e-14	.71	.14	-1.79487	54.3204	13.1832
12	.13	1.62284e-15	4.41047e-14	.71	.14	-1.79487	54.3204	13.1832
13	.13	1.62325e-15	4.41521e-14	.71	.14	-1.79487	54.3204	13.1832
14	.13	1.62328e-15	4.41564e-14	.71	.14	-1.79487	54.3204	13.1832
15	.13	1.62329e-15	4.41565e-14	.71	.14	-1.79487	54.3204	13.1832

Equilibrium mole fractions in the order CH_4, CO, CO_2, H_2, H_2O are:
.132653   1.65641e-15   4.50576e-14   .72449   .142857

The number of moles of gas = 1. per mole of original gas
The volume = .820569 liters per mole of original gas
now at end

APPENDIX 1

SYMBOLS - TEXT

A	Helholtz energy of the system
C	Number of components
E_j	Number of gram atoms of element j
F	Number of degrees of freedom
F_A	Function actually minimized for constant volume problems
F_G	Function actually minimized for constant pressure problems
G	Gibbs energy of the system
G^o	Gibbs energy of the chemical elements
J	Jacobian of the functions set equal to zero for minimization
J^{-1}	Inverse of J
L_j	Function expressing conservation of element j
N	Number of chemical species
P	Number of phases (discussion of phase rule only)
P	Pressure of the system
	Number of independent chemical reactions (subsection Checking the Estimates for Stopping Only)
R	Universal gas constant
T	Thermodynamic temperature
V	Volume of the system
a_i	Coefficients in the empirical equation for $\ln k_i$
b_i	Coefficients in the empirical equation for the natural logarithm of the vapor pressure of water
c	Number of gram atoms of carbon in the system
e	Number of chemical elements in the system
f_t	Value at the t-th iteration of the functions set equal to zero for minimization
g	Number of gaseous substances
h	Number of gram atoms of hydrogen in the system
k_f	Equilibrium constant of formation of $A_x B_y$
k_i	Equilibrium constant of formation of the i-th substance
k_t	Value of weighting factor k for t-th trial
$\ln$	Natural logarithm
m	Maximum exponent of temperature in equations for equilibrium constants of formation and vapor pressure of water
n_c	Number of moles of solid carbon
n_g	Total number of moles of gas
n_i	Number of moles of the i-th substance
o	Number of gram atoms of oxygen in the system
p_i	Partial pressure of substance i
p_s	Saturated vapor pressure of water
s	Total number of substances
t	Number of trial or interation
x,y	Coefficients and subscripts in chemical equation of formation of $A_x B_y$

x_t	Vector representing the variables being estimated at iteration number t
ΔG_f°	Gibbs energy of formation of one mole of $A_x B_y$ with all substances in the standard states
Γ_A	Function of A which is minimized
Γ_G	Function of G which is minimized
λ_j	Lagrangian multiplier
μ_i^j	Chemical potential, partial molar Gibbs energy of the i-th substance

APPENDIX 2

SYMBOLS - PROGRAM

$I(i,j)$	Inverse of the Jacobian, J
$J(i,j)$	Jacobian
$N(i,t1)$	Number of moles of the i-th substance for the t-th trial
a$	"Yes" or "no" to query about choosing case
a,b,d,e	Constants used to differentiate functions for the cases
b$	"Yes" or "no" to query about choosing initial estimates
c	Number of gram atoms of carbon in the system
c$	"p" or "v" for constant pressure or constant volume problem
$c(i,1)$	Unweighted correction to the i-th variable
$c(i)$$	Case number i as a string variable
c1	Case number during an iteration set
c2	Case number found as a result of iterations
d$	"l" or "s" for length of printout desired
d1	Relative difference between saturated vapor pressure of water and partial pressure of water calculated from mole fraction found by iteration
$f(i,1)$	The i-th function being set equal to zero
fnc	Carbon function
fnw	Water function
g	Original number of moles of gas
$g(t1)$	Number of moles of gas
h	Number of gram atoms of hydrogen in the system
k	Weighting factor for applying corrections
k_1, k_2, k_3	Equilibrium constants for the three independent reactions calculated from the logarithms of the equilibrium constants of formation
k_4, k_5, k_6	Equilibrium constants for the three independent reactions calculated from mole fractions found by iteration
$l(i)$	Natural logarithm of equilibrium constant of formation of the i-th substance
n	Size of the pertinent Jacobian
o	Number of gram atoms of oxygen in the system
p	Pressure in atmospheres
p$	Pressure as a string variable
$p(t1)$	Pressure of a constant volume system at the t1-th trial
p0	Initial pressure in a constant volume system
r	Universal gas constant
s	Number of sets of iterations performed
t	Temperature in kelvins
t$	Temperature as a string variable
t0,t9	Starting and ending indexes for the iteration loop

t_1	Number of an iteration
t_2	Square of t
t_3	Cube of t
t_4	Fourth power of t
v	Volume
v0	Initial volume in a constant pressure system
x(i)	Mole fraction of the i-th gaseous substance

APPENDIX 3

LISTING

```
100'      colgas    WSHorton    9/7/77
110' Calculates equilibrium composition for the CH4, CO, CO2, H2, H2O
     system
120' by minimizing the Gibbs energy for a constant pressure problem or the
130' Helmolz energy for a constant volume problem.
140'
150' Initial Statements
160'
170width80
180randomize
190dimg(150),I(15,15),J(15,15),N(15,150),p(150)
200deffnw=2*n(6,tl-1)+n(7,tl-1)-1(6)
210deffnc=c-n(1,tl-1)-n(2,tl-1)-n(3,tl-1)
220r=.08205686' V-zero = 24.41383e-3m↑3mole↑-1
230c(1)$="I"
240c(2)$="II"
250c(3)$="III"
260c(4)$="IV"
270'
280' Input
290'
300print"Is this a constant pressure (p), or a constant volume (v) problem,"
310print"and do you want a short (s) or a long (l) printout";
320inputc$,d$
330print"What are the temperature (kelvins) and";
340ifc$="p"orc$="P"then380
350print" volume (liters)";
360inputt$,v
370goto400
380print" pressure (atmospheres)";
390inputt$,p$
400ift$(1,1)="*"then430
410t=val(t$)
420goto440
430t=val(t$(2))+273.15
440print"Temperature ="t;"K =";t-273.15;"C"
450ifc$="p"orc$="P"then 480
460print"Volume ="v;"liters"
470goto530
480ifp$(1,1)="*"then510
490p=val(p$)
500goto520
510p=val(p$(2))/.10325
520print"Pressure  ="p;"atm =";p*0.101325;"MPa"
530print
540print"What are the assumed concentrations in mole fractions of the gases"
```

```
550print"in the order: CH4, CO, CO2, H2, and H2O";
560inputn(1,0),n(2,0),n(3,0),n(4,0),n(5,0)
570g=g(0)=n(1,0)+n(2,0)+n(3,0)+n(4,0)+n(5,0)
580c=n(1,0)+n(2,0)+n(3,0)
590h=4*n(1,0)+2*n(4,0)+2*n(5,0)
600o=n(2,0)+2*n(3,0)+n(5,0)
610ifc¢<>0andh¢<>0ando¢<>0then650
620print"It is necessary to have compounds containing carbon, oxygen,"
630print"and hydrogen.   Please try again."
640goto540
650ifn(1,0)+n(2,0)+n(4,0)¢<>0then680
660print"Carbon dioxide and water alone do not react significantly"
670goto3850'   print,end
680fori=1to5
690  printn(i,0);
700  ifn(i,0)<>0then720
710  n(i,0)=1e-7
720nexti
730print
740print
750ifc$="p"orc$="P"then810
760a=0
770p=p0=r*t/v
780p(0)=g(0)*p0'  Initial estimate of pressure
790print"The initial pressure ="p(0);"atm per mole of original gas"
800goto840
810a=1
820v0=r*t/p'      Initial  volume
830print"The initial volume ="v0;"liters per mole of original gas"
840print
850print"Gas contains C, H, and O atoms in the proportions"c;","h;", and"o
860ifd$="s"ord$="S"then970
870print"Do you want to choose the starting case";
880inputa$
890printa$
900ifa$="no"then960
910print"What case number";
920inputc1
930print"Case number"c1
940print
950goto990
960print
970c1=0'  Causes bypass of line 1530
980ifd$="s"ord$="S"then1180
990print"Do you want to provide your own initial estimates";
1000inputb$
1010printb$
1020print
1030ifb$="yes"then1050
1040goto1090
```

```
1050print"What are they in the same order as above";
1060inputn(1,0),n(2,0),n(3,0),n(4,0),n(5,0)
1070printn(1,0);n(2,0);n(3,0);n(4,0);n(5,0)
1080print
1090print" 0";
1100g(0)=0
1110fori=1to5
1120   printn(i,0);
1130   ifn(i,0)<>0then1150
1140   n(i,t1)=10↓(-7-int(4*rnd))
1150   g(0)=g(0)+n(i,0)
1160nexti
1170print
1180n(6,0)=n(7,0)=n(8,0)=n(9,0)=0
1190'
1200' Thermodynamic Data
1210'
1220t2=t*t
1230t3=t*t2
1240t4=t2*t2
1250ℓ(1)=8212.35/t-.816063*log(t)-1.00801e-2*t+7.73804e-6*t2
1260ℓ(1)=ℓ(1)-3.06981e-9*t3+5.08552e-13*t4
1270ℓ(2)=13632.3/t+1.8055*log(t)-.0023936*t+3.72836e-7*t2
1280ℓ(3)=47326.7/t+.0777872*log(t)-2.80706e-4*t+3.48747e-8*t2
1290ℓ(4)=0
1300ℓ(5)=28786.6/t-.697311*log(t)-.00145957*t+8.3769e-7*t2-1.80285e-10*t3
1310ℓ(7)=55.5049-9430.74/t-.159684*t+3.07499e-4*t2-3.0549e-7*t3+1.24325e-10*t4
1320ℓ(6)=1(5)-1(7)
1330k1=exp(ℓ(2)+ℓ(5)-ℓ(3)-ℓ(4))
1340k2=exp(ℓ(1)+ℓ(5)-ℓ(2)-3*ℓ(4))
1350k3=exp(2*ℓ(2)-ℓ(3))
1360fori=1to5
1370   m(i)=log(p)-ℓ(i)
1380nexti
1390'
1400' Assign max. size and constant elements of basic Jacobian
1410'
1420n=9
1430matJ=zer(n,n)
1440J(2,7)=J(7,2)=J(5,7)=J(7,5)=1
1450J(3,7)=J(7,3)=J(4,6)=J(6,4)=J(5,6)=J(6,5)=2
1460J(1,6)=J(6,1)=4
1470'
1480' Assign constants for first set of iterations
1490'
1500s=0
1510t0=1
1520t9=30
1530onc1goto1630,1790,1920,2080
1540'
```

```
1550' Test for possibility of liquid water"
1560'
1570ift<647.3andp>exp(ℓ(7))then1600
1580cl=2
1590goto1790
1600cl=4
1610goto2080
1620'
1630' Case I
1640'
1650ifs>0then1680
1660ifd$="s"ord$="S"then1680
1670printn(6,0);n(7,0);n(8,0)
1680b=e=0
1690d=1
1700n=8
1710J(6,8)=J(8,6)=2
1720J(7,8)=J(8,7)=1
1730ifd$="s"ord$="S"then1770
1740print
1750print"Case I"
1760print
1770goto2220' iterate
1780'
1790' Case II
1800'
1810ifs>0then1840
1820ifd$="s"ord$="S"then1840
1830printn(6,0);n(7,0)
1840b=d=e=0
1850n=7
1860ifd$="s"ord$="S"then1900
1870print
1880print"Case II"
1890print
1900goto2220' iterate
1910'
1920' Case III
1930'
1940ifs>0then1970
1950ifd$="s"ord$="S"then1970
1960printn(6,0);n(7,0);n(8,0);n(9,0)
1970b=d=1
1980e=n=9
1990J(6,8)=J(8,6)=2
2000J(7,8)=J(8,7)=1
2010J(1,9)=J(9,1)=J(2,9)=J(9,2)=J(3,9)=J(9,3)=1
2020ifd$="s"ord$="S"then2060
2030print
2040print"Case III"
```

```
2050print
2060goto2220' iterate
2070'
2080' Case IV
2090'
2100ifs>0then2130
2110ifd$="s"ord$="S"then2130
2120printn(6,0);n(7,0);n(8,0)
2130b=1
2140d=0
2150e=n=8
2160J(1,8)=J(8,1)=J(2,8)=J(8,2)=J(3,8)=J(8,3)=1
2170ifd$="s"ord$="S"then2220
2180print
2190print"Case IV"
2200print
2210'
2220' Newton-Raphson Iterations
2230'
2240fortl=t0tot9
2250   f(1,1)=log(n(1,tl-1))-a*log(g(tl-1))+4*n(6,tl-1)+b*n(e,tl-1)+m(1)
2260   f(2,1)=log(n(2,tl-1))-a*log(g(tl-1))+n(7,tl-1)+b*n(e,tl-1)+m(2)
2270   f(3,1)=log(n(3,tl-1))-a*log(g(tl-1))+2*n(7,tl-1)+b*n(e,tl-1)+m(3)
2280   f(4,1)=log(n(4,tl-1))-a*log(g(tl-1))+2*n(6,tl-1)+m(4)
2290   f(5,1)=log(n(5,tl-1))-a*log(g(tl-1))+2*n(6,tl-1)+n(7,tl-1)+m(5)
2300   f(6,1)=4*n(1,tl-1)+2*n(4,tl-1)+2*n(5,tl-1)+d*2*n(8,tl-1)-h
2310   f(7,1)=n(2,tl-1)+2*n(3,tl-1)+n(5,tl-1)+d*n(8,tl-1)-o
2320   onclgoto2330,2390,2350,2380
2330   f(8,1)=fnw
2340   goto2390
2350   f(8,1)=fnw
2360   f(9,1)=-fnc
2370   goto2390
2380   f(8,1)=-fnc
2390   ifc$="p"orc$="P"then2440
2400   fori=1to5
2410     J(i,i)=1/n(i,tl-1)
2420   nexti
2430   goto2520
2440   fori=1to5
2450     forj=1to5
2460       ifi=jthen2490
2470       J(i,J)=-1/g(tl-1)
2480       goto2500
2490       J(i,i)=1/n(i,tl-1)-1/g(tl-1)
2500     nextj
2510   nexti
2520   matI(n,n)=inv(J(n,n))
2530   matc(n,1)=I(n,n)*f(n,1)
2540   ifd$="s"ord$="S"then2560
```

```
2550   printtl;
2560   fori=lton
2570     ifi>5then2610
2580     iftl>15then2610
2590     k=sin((tl-8)*&pi/16)/2+1/2
2600     goto2620
2610     k=1
2620     n(i,tl)=n(i,tl-1)-k*c(i,1)
2630     ifn(i,tl)>0then2660
2640     ifi>5then2660
2650     n(i,tl)=10↑(-7-int(4*rnd))
2660     ifd$="s"ord$="S"then2680
2670     printn(i,tl);
2680   nexti
2690   ifd$="s"ord$="S"then2710
2700   print
2710   g(tl)=n(1,tl)+n(2,tl)+n(3,tl)+n(4,tl)+n(5,tl)
2720   ifc$="p"orc$="P"then2740
2730   p=p(tl)=g(tl)*p0
2740   fori=lton
2750     ifabs(c(i,1)/n(i,tl))>5e-5then2780
2760   nexti
2770   goto2880
2780nexttl
2790tl=tl-1
2800printtl;" iterations did not converge!"
2810fori=1to5
2820   x(i)=n(i,tl)/g(tl)
2830nexti
2840k4=x(2)*x(5)/(x(3)*x(4))'          CO2 + H2 = CO + H2O
2850k5=x(1)*x(5)/(x(2)*x(4)↓3*p*p)'  CO + 3H2 = CH4 + H2O
2860k6=x(2)*x(2)*p/x(3)'              CO2 + C(s) = 2CO
2870goto3270
2880s=s+1
2890'
2900' Case-consistency checking
2910'
2920fori=1to5
2930   x(i)=n(i,tl)/g(tl)
2940nexti
2950k4=x(2)*x(5)/(x(3)*x(4))'          CO2 + H2 = CO + H2O
2960k5=x(1)*x(5)/(x(2)*x(4)↓3*p*p)'  CO + 3H2 = CH4 + H2O
2970k6=x(2)*x(2)*p/x(3)'              CO2 + C(s) = 2CO
2980d]=(x(5)*p-exp(1(7)))/exp(1(7))'  H2O: (p.p. - v.p.)/v.p.
2990ifcl>2then3030
3000iffnc>0then3050
3010c2=2
3020goto3060
3030ifk6>k3then3050
3040goto3010
```

```
3050c2=0
3060onclgoto3070,3090,3070,3090
3070ifn(8,t1)>0then3120
3080goto3100
3090ifx(5)*p>exp(ℓ(7))then3120
3100c2=c2+2
3110goto3130
3120c2=c2+1
3130ifc2=c1then3340' successful exit
3140ifs>3then3250' unsuccessful exit; four inconsistent sets of iterations
3150c1=c2
3160fori=8ton
3170  forj=1ton
3180    J(i,J)=J(J,i)=0
3190  nextj
3200nexti
3210onclgoto1630,1790,1920,2080
3220'
3230' Output
3240'
3250print"Could not determine correct case with four sets of iterations"
3260print
3270print"The results at this stage are as follows"
3280print"Case "c(c1)$
3290print"The last set of estimates is, moles and multipliers:"
3300fori=1ton
3310  printn(i,t1);
3320nexti
3330print
3340print
3350print"Equilibrium mole fractions in the order CH4, CO, CO2, H2, H2O are:"
3360fori=1to5
3370  ifd$="ℓ"ord$="L"then3400
3380  printusing".####   ",x(i);
3390  goto3410
3400  printx(i);
3410nexti
3420print
3430print
3440ifd$="1"ord$="L"then3470
3450printusing"The number of moles of gas = #.#### per mole of original gas",g(t
1)/g
3460goto3480
3470print"The number of moles of gas ="g(t1)/g;"per mole of original gas"
3480ifc$="p"orc$="P"then3510
3490print"The pressure ="g(t1)*p0/g;"atm = ".101325*g(t1)*p0/g;
"MPa per mole of original gas"
3500goto3520
3510print"The volume ="g(t1)*v0/g;" liters per mole of original gas"
3520print
```

```
3530oncgoto3540,3540,3590,3630
3540ifd$="ℓ"ord$="L"then3570
3550printusing"Solid carbon is present in the amount of #.#### moles per mole of
 original gas",fnc/g
3560goto3580
3570print"Solid carbon is present in the amount of "fnc/g;"moles per mole of original
  gas"
3580ifC1=2then3630
3590ifd$="ℓ" or d$="L"then3620
3600printusing"Liquid water is present in the amount of #.#### moles per mole of
 original gas",n(8,t1)/g(0)
3610goto3630
3620print"Liquid water is present in the amount of "n(8,t1)/g;"moles
 per mole of original gas"
3630print
3640ifabs(k4-k1)/k1>1e-4then3710
3650ifabs(k5-k2)/k2>1e-4then3710
3660onc1goto3670,3670,3690,3690
3670ifabs(k6-k3)/k3>1e-4then3710
3680goto3750
3690if(k3-k3)/k3>1e-4then3710
3700goto3750
3710print"Equilibrium constants do not check out"
3720print"First equilibrium constant ="k1;"vs."k4
3730print"Second equilibrium constant ="k2;"vs."k5
3740print"Third equilibrium constant ="k3;"vs."k6
3750ift>647.3then3840
3760onc1goto3770,3790,3770,3790
3770ifabs(d1)>5e-5then3800
3780goto3850
3790ifd1<5e-5then3850
3800print"Relationship of H2O partial pressure and vapor pressure is wrong"
3810print"Vapor pressure of water ="exp(ℓ(7))
3820print"Partial pressure of water ="p*x(5)
3830goto3850
3840print"Above the critical temperature for water"
3850print
3860'end
```

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FEDERAL INFORMATION PROCESSING STANDARD SOFTWARE SUMMARY

01. Summary date			02. Summary prepared by (Name and Phone)	03. Summary action		
Yr.	Mo.	Day	W. S. Horton (301) 921-2859	New	Replacement	Deletion

01. Summary date			02. / 05.	03.

01. Summary date
Yr. 7 8 | Mo. 0 8 | Day 0 4

02. Summary prepared by (Name and Phone)
W. S. Horton (301) 921-2859

05. Software title
BASIC Computer Program for Calculating Simple Coal Gasification Equilibria

04. Software date
Yr. 7 8 | Mo. 0 4 | Day 1 4

03. Summary action
New [X]   Replacement [ ]   Deletion [ ]
Previous Internal Software ID

07. Internal Software ID
N.A.

06. Short title COLGAS

08. Software type	09. Processing mode	10. Application area		
		General		**Specific**
Automated Data System [ ]	Interactive [X]	Computer Systems Support/Utility [ ]	Management/ Business [ ]	Chemical Equilibria
Computer Program [X]	Batch [ ]	Scientific/Engineering [X]	Process Control [ ]	
Subroutine/Module [ ]	Combination [ ]	Bibliographic/Textual [ ]	Other [ ]	

11. Submitting organization and address
Center for Materials Science
National Bureau of Standards
Washington, D. C.   20234

12. Technical contact(s) and phone
W. S. Horton
(301) 921-2859

13. Narrative

COLGAS calculates the concentrations of gases and amounts of solid carbon and/or liquid water at equilibrium for constituents found in coal gasification plants. The gases are restricted to methane, carbon monoxide, carbon dioxide, hydrogen, and water and are considered to be ideal. Minimization of Gibbs energy is achieved by setting partial derivatives equal to zero and solving the resulting nonlinear equations by the Newton-Raphson technique.

14. Keywords
BASIC; carbon; carbon dioxide; carbon monoxide; coal gasification; COLGAS; hydrogen; interactive computer program; methane; minization of Gibbs energy; phase rule; simultaneous chemical equilibria; water

15. Computer manuf'r and model	16. Computer operating system	17. Programing language(s)	18. Number of source program statements
UNIVAC 1108	CSTS-Release 18	BASIC	377

19. Computer memory requirements	20. Tape drives	21. Disk/Drum units	22. Terminals
Program only: 10K	None	None	one, time-sharing, 110 or 300 baud

23. Other operational requirements
None

24. Software availability			25. Documentation availability		
Available [ ]	Limited [ ]	In-house only [X]	Available [X]	Inadequate [ ]	In-house only [ ]

26. FOR SUBMITTING ORGANIZATION USE
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4. TITLE AND SUBTITLE An Algorithm and BASIC Computer Program for Calculating Simple Coal Gasification Equilibria	5. Publication Date
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7. AUTHOR(S) William S. Horton	8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234	10. Project/Task/Work Unit No.
	11. Contract/Grant No.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Calculation of the equilibrium composition for the gases CH_4, CO, CO_2, H_2, and H_2O is treated by minimizing the Gibbs energy, G. Minimization is constrained by the conservation of chemical elements. With the use of Lagrangian multipliers, the minimum is found by setting the partial derivatives of G with respect to the amount of each substance equal to zero. The resulting non-linear equations are solved iteratively by the Newton-Raphson method. This algorithm is implemented with an interactive computer program written in the BASIC language and named COLGAS. The aim of this work was to provide people who test materials in coal-gasification-like atmospheres an easy way to obtain the equilibrium composition of their gas mixtures. A knowledge of computer programming is not required in order to use the program. A listing of the program is given and also six sample computer calculations. The phase rule is applied to the C-H-O system and two ternary diagrams are shown illustrating the condensation of solid carbon and liquid water.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

BASIC; carbon; carbon dioxide; carbon monoxide; coal gasification; COLGAS; hydrogen; interactive computer program; methane; minimization of Gibbs energy; phase rule; simultaneous chemical equilibria; water

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